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THE INDUSTRIAL CHEMISTRY
OF THE
FATS AND WAXES

THE
INDUSTRIAL CHEMISTRY
OF THE
FATS AND WAXES

BY

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SECOND EDITION, REVISED AND ENLARGED



LONDON
BAILLIÈRE, TINDALL AND COX
7 AND 8, HENRIETTA STREET, COVENT GARDEN, W.C.2

1941

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PRINTED IN GREAT BRITAIN

P R E F A C E T O T H E S E C O N D E D I T I O N

THE present edition of "Industrial Fats and Waxes" is now published as a separate monograph, and not as one of a series of textbooks on industrial chemistry. It is somewhat longer than the original edition, since in the interval between the publication of the two books there have been a number of technological developments which demand notice, and an even greater extension in knowledge of the composition of natural fats and waxes, and of the chemical properties and behaviour of certain groups of fats utilized in one or other of the industries which depend upon these raw materials. Whilst the general plan of the volume has been left unaltered, it has therefore been necessary to modify or to add to some of the contents of its chapters.

It has been possible to give much more positive information than formerly as to the kind and proportions of individual fatty acids present in the fats of technical utility or potential interest, and also as to the more prominent specific glycerides which occur in these materials. Moreover, on the chemical side, important advances have been made in some technically useful methods of analysis, and also, especially, in further understanding of the processes which go on during the oxidation and the polymerization of the more unsaturated fats.

The chief new additions to fat technology are, perhaps, the development of a large number of semi-synthetic detergents in which the carboxylic acids of the fatty soaps are replaced most often by salts of sulphates or sulphonates of long-chain carbon compounds (although basic (ammonium) or neutral types of compound have also been proposed);

the utilization of fresh fatty oils, of semi-synthetic drying oils, and of synthetic resins in the paint and varnish industries ; improvements in margarine making this product, nutritionally and in physical properties, more nearly the equivalent of butter and superior to the latter in resistance to oxidative rancidity ; and important, although not fundamental, improvements in the extraction and refining of fatty oils. The use of higher vacua and of acid-resisting metals in plant construction has contributed much to technical progress in such matters as deacidification and deodorization of fats.

It is hoped that all these changes find adequate reference, in due perspective, and that the volume may continue to serve as a general guide to the principles and procedure of the important industries which depend upon the natural fats.

My cordial thanks are accorded to Miss M. Tadman, M.Sc., for valued assistance in preparing the revised manuscript and index, and in correcting the proofs of the present edition.

T. P. H.

UNIVERSITY OF LIVERPOOL,

May, 1941.

PREFACE TO THE FIRST EDITION

To give a connected and logical account of the chemical aspects of the diverse industries based upon natural fats and waxes within reasonable limits of space is a difficult, if not a thankless task. The objectives of the present volume have been to treat the subject, following the general scheme of this series of text-books, in such a way as to afford an introduction to the chemical technology involved, to survey the whole of the outlets for fats and waxes with due regard to perspective, and to emphasize throughout the connection between the chemical constitution of the raw material and the particular economic application in view.

Whilst the author has perhaps had largely in mind the needs of the college or technical school student who has, or proposes to, become engaged in fat technology, the book is intended equally for reference by others already familiar with one or other of the industries discussed, and it is hoped also that it may serve to indicate avenues of potentially useful investigation.

The varied industries concerned with fats and waxes are perhaps differentiated from any others in that they are based, not on the same raw material, but on a single class of raw materials which, although in one sense closely chemically related, embrace a wide variety of characteristics. It is therefore the more important to comprehend to the fullest extent the chemical constitution and relationships of the natural fats and waxes, and the first two sections of the volume are given over to this fundamental side of the subject. On the other hand, it has not been possible, in general, to deal in full detail either with engineering and

plant construction, or with the more intricate side of analytical procedure. Standard handbooks are available in which these matters are dealt with *in extenso* and references are given in the sectional bibliographies to the appropriate works, which should enable the reader to obtain specialized data where necessary.

For the same reason, and in order not to increase the size of the book unduly, free use has been made of tables where possible, and illustrations and diagrams have been dispensed with. As regards the latter, it seemed that the only useful alternatives were complete exclusion or the provision of a very considerable number, and accordingly an attempt has been made to give as graphical a description as possible of the apparatus involved without recourse to pictorial illustration.

Most of the standard works of reference, and also of the original communications, to which reference is made in the bibliographies have been consulted during the compilation of the present work, and the author has received much helpful criticism and advice from Dr. E. Frankland Armstrong, F.R.S. (who contributed an Introduction to the first edition), Colonel E. Briggs, and Professor I. M. Heilbron, to all of whom grateful acknowledgments are offered ; whilst he desires to thank Messrs. J. Bruhl, A. Houlbrooke, B.Sc., and the Editor of the Industrial Chemistry Series for valued assistance whilst the book was in the press.

T. P. H.

UNIVERSITY OF LIVERPOOL,

June, 1927.

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INDUSTRIAL FATS AND WAXES

SECTION I.—THE CHEMICAL NATURE OF FATS

CHAPTER I.—INTRODUCTORY: THE NATURAL PROCESSES CONCERNED IN THE PRO- DUCTION OF FATS

THE extensive group of natural products embodied within the conventional term "oils, fats, and waxes" forms the raw material of a further series of derived substances which not only play a part in a wide variety of industries, but enter into daily life at many points.

Undoubtedly the most important use of the fats is in nutrition : the edible fat industry includes the production of milk-butter, lard, etc., as well as edible material produced by refining other animal and some vegetable fats from many different sources, and is indispensable to the civilization of the present day. Furthermore, certain specific oils such as castor, cod liver, and chaulmoogra oil have important medicinal uses.

From a national point of view the next most valuable feature of the fats is as a source of cleansing materials in the form of the soaps ; whilst in the course of the manufacture of the latter from fats there is also produced glycerine, valuable medicinally and otherwise, and essential to the explosives industry in the form of nitroglycerine.

Formerly the fats were largely used as a means of lighting, but have naturally been displaced by the more

modern systems of gas and electric light. The candles of the present day are mainly composed of solid paraffin hydrocarbons, admixed with some tallow acids; and the liquid fats such as colza oil which were once used in lamps have, at least in Western Europe and America, been almost entirely replaced by kerosene.

Fats and certain fatty derivatives are useful in some types of lubricating oils, whilst in the paint, varnish, and linoleum industries the peculiar "drying" properties of linseed oil and of a few other fatty oils create a consistent and considerable demand for liquid fats of this type. Specific types of liquid fats, and of chemical derivatives of fatty compounds, are also in industrial demand in the industries connected with canvas coverings and leather and in the dyeing and other processing of certain textiles.

Again, the species of fats known as waxes are in many instances valuable for polishes of various kinds.

The present volume has not been written solely in order to describe the industrial processes into which "oils, fats, and waxes" enter, nor to discuss the simple chemical properties of the latter; it is rather concerned to show as far as possible how the chemical constitution of definite fats is connected with particular utility either of the fat or of its constituent fatty acids in different industries. Moreover, the wider problems of the conservation and the development of natural fat resources suitable for application in these diverse directions are subjects which should always be present in the minds of those who specialize in this field of applied chemistry.

The fats are, in the simplest terms, naturally occurring esters of the higher, saturated or unsaturated, paraffin monocarboxylic acids; these acids are combined most usually with the trihydric alcohol glycerol, but also in quite large amounts with alcohols of closely similar structure to the acids or with other alcohols of a more complex type, such as cholesterols or phytosterols. When the combined alcohol is not glycerol but one of the other types, and especially if it is a member of the higher saturated paraffinoid

series mentioned, the resulting ester is hard and non-greasy to the touch—in other words, it is a “wax” rather than a “fat.”

From the chemical standpoint, however, it seems well to embrace the whole group of natural products within the term “fat,” reserving the sub-grouping “wax” for fatty materials which are not greasy to the touch and which do not contain glycerol as the alcoholic part of the molecule.

Frequently, of course, the phrase “oils, fats, and waxes” is used to cover, respectively, (i) those fats which are liquid at the ordinary temperature, (ii) those which are semi-solid or solid, but typically greasy to the touch, and (iii) the solid fats which are non-greasy and contain no combined glycerol.

The term “oil,” however, is a very general one used equally for the mineral oils or hydrocarbons, the essential oils or terpene derivatives and the liquid fats; it appears to the writer that it would be well to discontinue its employment in the case of the fats and refer to the foregoing classes respectively as liquid fats, solid fats, and waxes—a course which will be pursued in this work in so far as convention permits.

It may be recalled, in passing, that a number of more or less successful attempts have been made to manufacture fatty acids from the hydrocarbon or mineral oils (*cf.* Section II., Chapter IV.); but, whilst under the stress of quite abnormal conditions such products may acquire some measure of utility, it must be remembered that for most purposes fats of particular qualities are employed, and the synthetic fatty acids from petroleum are not likely ever to be obtained in the wide variety of specific qualities which are characteristic of the natural materials. Moreover, petroleum supplies are, ultimately, drawn from a source which, like a mineral deposit, is definitely limited, even though it be of a large order of magnitude; whereas the natural fats are producible in recurrent crops which at present yield several millions of tons of fats each year, and which are capable of development to a much greater

extent. Also, it is, in the writer's opinion, much more probable that fats of desired specific properties may be produced *in vivo* as a result of joint investigations of chemists, botanists, and zoologists than by the purely chemical oxidation and transformation of the very complex mixture of hydrocarbons present in petroleum.

The Natural Processes concerned in the Production of Fats.—It is only necessary, for the purpose of the present work, to indicate briefly what is known at present of the means whereby the fats are synthesized in living matter.

In plants and animals the fats are normally a form of reserve or storage of organic matter which at a later stage in the life-cycle may be required for purposes of nutrition.

The primary seat of the production of fats is in the vegetable kingdom; here the carbohydrate materials produced in the plant from carbonic acid and water by the agency of enzymes and sunlight are converted into fatty compounds, mainly at the period of ripening of the seed and fruit. The fats are deposited in general either in the tissue which surrounds the embryo or germ of the seed (the endosperm), or in the external fleshy covering or pericarp, in which in many cases the seed-capsule is enclosed.

The fatty matter of the kernel or endosperm is utilized during germination of the seed, at which point it may be retransformed into sacchariferous compounds.

It is interesting to note that, although in their natural condition the fats of a ripe seed contain little or no free acid, the work of Eyre, Ivanow and others has indicated that fatty acids themselves are synthesized in the fruit prior to the production of neutral ester (glyceride). When the ripening process is complete, however, the fats are present almost exclusively in the form of glyceryl (or other) esters.

The nature of the fat which is thus stored in or near the seed of the plant depends on numerous factors which are as yet but imperfectly understood; doubtless the kind of carbohydrate material (or possibly, in some cases, terpene material) from which the fat is derived is an important

factor, together with the climatic conditions in which the plant thrives, and, above all, the biological factors which determine the individuality of the plant species concerned.

In animals, fats are produced by assimilation of other fats as food as well as by vital synthesis from other types of organic matter, such as carbohydrates and possibly also proteins.

The formation of fats in the animal body is believed to take place mainly in the liver and related organs ; here the primary organic materials are converted into fatty acids and their esters, whilst fat already present as such may be hydrolysed and re-built up into esters with or without alteration in the constitution of the fatty acids originally ingested ; and the synthesized fat passes via the blood-stream into various parts of the body—notably the flesh-tissues near the skin—in which it is stored.

The reader is referred to the biochemical monographs of Leathes and Raper, Armstrong, Maclean, etc., for further information on the origin of fats in the living organism. Consideration of the components of the various classes of fats and waxes described in Section II. (pp. 99–176) and of the manner in which, in Nature, there exists a wide diversity of selected types of fat reserves, based nevertheless on a few simple patterns of closely-related chemical structure, will show that the fundamental questions of plant metabolism and vital synthesis are of primary importance and intense interest ; but these matters are outside the province of the present work.

CHAPTER II.—THE PROPERTIES AND STRUCTURE OF THE FATTY ACIDS IN NATURAL FATS AND WAXES

General.—In this and the succeeding chapter the chief characteristics of the compounds which are the component units of the fats and waxes will be briefly described, since in order to understand the reasons for their diverse technical uses it is necessary in the first place to know something of their chemical nature.

The properties of the fats or glycerides, more especially, are very definitely associated with the fatty acids of which they are esters. Broadly speaking, these fall into two classes, the saturated and the unsaturated fatty acids ; both consist of long chains of carbon atoms strung together with an acidic or carboxyl ($-COOH$) group at one end of the molecule. In nearly all cases the carbon chains are consecutive ; in other words, each carbon atom is attached only to two other carbon atoms, the remaining valencies being satisfied by hydrogen atoms or left in some cases unsatisfied (ethylenic linkage).

The majority of the fatty acids are thus " straight-chain " aliphatic compounds, although there are a few cases in which the carbon chain is " branched," *i.e.* one or more carbon atoms may be united with three or perhaps even four other carbon atoms ; also, a few acids in certain fats contain some of the carbon atoms linked up to form a closed chain or ring system, but in these instances there is also present a fairly long " straight chain " of carbon atoms. Either branched-chain or closed-chain fatty acids are, however, definitely exceptional : the overwhelming majority of the

acids present in natural fats and waxes are saturated or unsaturated straight-chain monocarboxylic acids.

Another curious and striking feature of the natural fatty acids is that almost, although not quite entirely, without exception, they contain an even number of carbon atoms. The apparent exceptions to this statement are *iso*-valeric acid, $C_6H_{10}O_2$, and "margaric acid," $C_{17}H_{34}O_2$, which have been reported to exist, the first in dolphin and porpoise oils and the second in tallow and lard; but the latter has been definitely shown to be an equimolecular mixture of palmitic and stearic acids which simulates a chemical individual. "Daturic acid," $C_{17}H_{34}O_2$, more recently stated to occur in datura oil, has been similarly shown to be the same mixture of palmitic and stearic acids.

The tendency for two different fatty acids to form an equimolecular complex is readily understood when we remember that the crystal unit of the solid fatty acids has been definitely shown by X-ray analysis to be made up of two molecules of fatty acid apparently arranged with their free acidic groups oriented towards each other, whereas the esters of the acids are monomolecular in the solid state. There is some evidence to show that the liquid (unsaturated) higher fatty acids also pass into a bimolecular form, at all events after standing for some little time, whilst the bimolecular nature of acetic acid has of course been recognized for a considerable period.

It is convenient to refer to the acids, saturated or unsaturated, according to the number of carbon atoms which they contain, and in this way it may be said that the great majority of the natural acids are of the C_{12} , C_{14} , C_{16} , C_{18} , C_{20} , and C_{22} series.

In any saturated acid, where each carbon atom other than that in the terminal carboxylic group ($-COOH$) and that in the other terminal group (CH_3-) is united to two carbon and two hydrogen atoms, the general formula will be $C_nH_{2n}O_2$, where n is an even number.

Unsaturated acids may contain two carbon atoms, each of which is only united to one hydrogen, the remaining

valencies of each of these atoms being unsaturated so that an " ethylenic linkage " or " double bond " results ; or there may be two or several pairs of unsaturated carbon atoms, leading to the presence of two or several ethylenic linkages. The general formulæ of these acids will thus be $C_nH_{2n-2}O_2$, $C_nH_{2n-4}O_2$, $C_nH_{2n-6}O_2$, etc.

Thus it will be seen that the fatty acids in a natural fat may comprise a possibly large number of different individuals closely resembling each other in molecular weight and general chemical constitution, and therefore in many physical properties, although the fundamental principles of their structure are exceedingly simple and straightforward. This renders their separation in the laboratory a matter of some difficulty, and special methods, described in Chapter V. of this section, have been worked out for this purpose.

Saturated Fatty Acids.—The more important naturally-occurring fatty acids and some of their chief characteristics are summarized in the following table :

Acid.	Formula.	Free acid.		Ref. index.	Methyl ester.		Ethyl ester.	
		M.p.	B.p.		M.p.	B.p.	M.p.	B.p.
n-Butyric	$C_4H_8O_2$	-8°	163°	1.3990 20°	102°		120°	
iso-Valeric	$C_5H_{10}O_2$	-51°	174°					
n-Caproic ..	$C_6H_{12}O_2$	-1°	205°	1.4164 20°	150°		167°	
n-Caprylic ..	$C_8H_{16}O_2$	16°	237°	1.4283 20°	-40°	194°	-47°	208°
n-Capric ..	$C_{10}H_{20}O_2$	31.3°	269°	1.4286 40°	-18°	224°		245°
n-Lauric ..	$C_{12}H_{24}O_2$	43.5°	102°/1 mm.	1.4267 60°	5°	87°/1 mm.	-10°	260°
n-Myristic ..	$C_{14}H_{28}O_2$	54.4°	122°/1 mm.	1.4308 60°	19°	111°/1 mm.	11°	295°
n-Palmitic ..	$C_{16}H_{32}O_2$	62.9°	139°/1 mm.	1.4234 60°	29°	130°/1 mm.	25°	143°/3 mm.
n-Stearic ..	$C_{18}H_{36}O_2$	69.6°	160°/1 mm.	1.4300 80°	38°	154°/1 mm.	31°	152°/0.2mm.
n-Arachidic ..	$C_{20}H_{40}O_2$	75.4°	205°/1 mm.		45°	180°/1 mm.	41°	177°/0.3mm.
n-Behenic ..	$C_{22}H_{44}O_2$	80.0°				52°	48°	185°/0.2mm.
n-Lignoceric ..	$C_{24}H_{48}O_2$	84.2°				58°		54°
n-Cerotic ..	$C_{26}H_{52}O_2$	87.7°				63°		60°

Some uncertainty existed until recently as to whether the arachidic and lignoceric acids occurring in small proportions in groundnut and some other fats were the normal straight-chain acids or isomeric branched-chain forms, because the melting points of these acids isolated from the

natural products were lower than those of the synthetic acids. By fractional distillation of a large quantity of the esters of the C₂₀, C₂₂, and C₂₄ acids of groundnut oil, Jantzen and Tiedcke obtained pure individual acids whose properties agreed with those of the synthetic normal acids, and it is now accepted that these natural acids possess the straight-chain structure. The previous uncertainty as to their identity was probably due to the difficulty of complete separation of small quantities of these higher fatty acids.

The constitution of all the straight-chain saturated acids up to *n*-hexatriacontanoic acid, C₃₆H₇₂O₂, is known from their synthetical preparation from the lower members. This was carried out in the case of the acids up to and including stearic acid by Schorlemmer, Lieben, Krafft and others, and for the higher acids by Levene and Taylor, and by Francis and Piper.

The steps in the modern synthesis employed by the latter workers were :

R . COOC₂H₅ reduced by sodium and alcohol to
R . CH₂OH ;

R . CH₂OH converted to the iodide R . CH₂I, and this to the cyanide R . CH₂CN ;

R . CH₂CN hydrolysed by alcoholic potash to
R . CH₂ . COOH.

The yields were over 90 per cent. of theoretical at each stage.

Direct syntheses of higher fatty acids of the even-numbered series, including lauric, myristic, palmitic and stearic acids, were not achieved until 1936, when Kuhn and others polymerized crotonaldehyde, CH₃ . CH : CH . CHO, into octatrienal, CH₃ . [CH : CH]₃ . CHO, dodecapentaenal, CH₃ . [CH : CH]₅ . CHO, and hexadecaheptaenal, CH₃ . [CH : CH]₇ . CHO. Reduction of the two latter compounds yielded respectively dodecyl (lauryl) and hexadecyl (cetyl) alcohols, which on oxidation give lauric and palmitic acids ; whilst condensation of either polyene aldehyde with malonic acid, followed by hydrogenation and decarboxylation of the products, led respectively to the syntheses of

myristic and stearic acids. These syntheses lead directly from acetaldehyde to the higher fatty acids with an even number of carbon atoms in the molecule.

The following points connected with individual saturated acids may be noted here :

n-Butyric acid is present in mixed glycerides in butter and in other milk fats to the extent of about 3-10 per cent., but does not occur in any other natural fat. Consequently the amount of water-soluble and comparatively volatile fatty acids present in the component fatty acids of an edible fat is a close indication of the amount of true butter present, pending the development of any process for the artificial introduction of butyryl into vegetable butters or other butter substitutes (*cf.* Reichert-Meissl value, this section, Chapter IV., p. 56).

Glycerides containing normal *caproic*, *caprylic*, and *capric* acids also occur in small proportions in milk fats, and in addition they are found in similar or even greater amounts (especially the capric esters) in coconut, palm kernel, and similar tropical nut oils.

The lower fatty acids are freely volatile in steam, but progressively less so as the molecular weight increases ; lauric acid is almost non-volatile in steam at atmospheric pressure, but capric, caprylic, and caproic acids are quite definitely volatile under these conditions. Consequently, like butter fats, the nut oils show a certain percentage of "volatile fatty acids" in the Reichert test (p. 58), but these are insoluble in water, thus differing from butyric acid. The Polenske modification of the Reichert-Meissl process of analysis (p. 57) differentiates between "soluble" (butyric) and "insoluble" (caproic, caprylic, capric) volatile fatty acids.

n-Lauric acid occurs abundantly in coconut, palm kernel, and the other tropical nut oils and forms about 20 per cent. of the fatty acids of sperm head oil. Its sodium salt is fairly soluble in water and lathers freely ; it is, in fact, the most useful of the saturated fatty acids as a soap constituent. The saturated acids of lower molecular weight than lauric

acid do not form true soaps when combined with soda, whilst the soaps of stearic and higher saturated acids are too sparingly soluble to be of much practical utility.

n-Myristic acid is widely distributed, but except in the nutmeg family it does not predominate in any individual fat. It occurs in small quantities in most tallow, to the extent of 5-10 per cent. in whale and fish oils and in the head oil of the sperm whale, in coconut and palm kernel oils.

n-Palmitic acid is not only widely distributed, but is almost certainly the most abundant of the natural saturated fatty acids.

It forms from 20 to 30 per cent. of the acids contained in butter fat, tallow, palm oil, cacao butter, cottonseed, and other oils, whilst it is present to the extent of about 3-10 per cent. in almost all the common vegetable fats, such as olive, linseed, soya bean, sunflower, or groundnut oils.

The acid, admixed with stearic acid, is a useful basis for tallow candles, and the sodium salt is a typical soap as regards lathering power but is inferior in solubility to the myristate and laurate.

n-Stearic acid is also widely distributed, but not in high proportion except in the lards and tallow (10-30 per cent.), cacao butter, and a few other fats. Although it is present in nearly all other natural fats, it only forms from about 1 to 5 per cent. at most of the total fatty acids present therein; the predominant acids containing 18 carbon atoms are the unsaturated *oleic* and *linoleic* acids (see below). Sodium stearate is a rather insoluble salt forming colloidal or "soap" solutions, but with very poor detergent properties at the ordinary temperature.

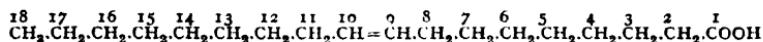
The saturated acids of higher molecular weight than stearic acid occur less frequently in nature. Arachidic and lignoceric acids occur in small quantities in groundnut oil, beechwood tar, and other fatty products, and in larger proportions (up to 25 per cent.) in a few specific vegetable fats, whilst cerotic and melissic acids are frequent components of vegetable and insect waxes. These acids are of no interest to the soap industry.

Unsaturated Fatty Acids.—The unsaturated fatty acids are of greater technical value and importance than the solid acids, in so far that many of the factors which render different fats of industrial importance are due to particular properties of their component unsaturated fatty acids. For example, ordinary oleic acid gives rise to the most widely useful constituent of soaps, sodium oleate ; linseed oil owes its exceptional "drying" power to the presence of suitable proportions of the more highly unsaturated glycerides of linoleic and linolenic acid ; fatty lubricants may, on the other hand, be largely composed of olein (*e.g.* neat's foot oil, rape seed oil), or again, may be of the highly viscous type represented by castor oil. Oils containing the more unsaturated glycerides, such as linolein, linolenin, or the very highly unsaturated glycerides of the marine animal oils, are of little use as lubricants because the unsaturated acids in question, whether free or as glycerides, rapidly absorb oxygen and become "gummy" ; whilst the glyceride olein of ordinary oleic acid does not absorb oxygen readily, and hence is of little use as a paint vehicle—it is a "non-drying" oil.

Practically all the unsaturated members which have been found in nature are known to be straight-chain acids, because on hydrogenation (*cf.* Section III., Chapter III., p. 241) they are converted into the normal straight-chain fatty acids, whose structure has been satisfactorily determined by synthesis.

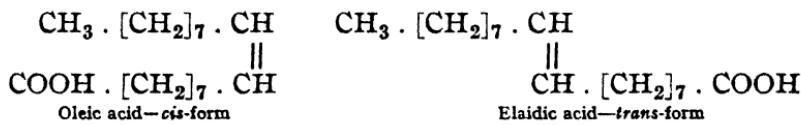
Synthetical work on the unsaturated higher fatty acids has only been carried out in a few cases. Robinson effected a partial synthesis of oleic acid in 1925, and a complete synthesis (leading to the equilibrium mixture of oleic and elaidic acids, p. 14) was later successfully achieved by Noller and Bannerot in 1934. Noller and Girvin subsequently attempted a similar synthesis of linoleic acid, which was obtained admixed with structurally isomeric products. The only other unsaturated higher fatty acid synthesized up to the present is the optically inactive (racemic) form of the natural *d*-chaulmoogric acid (Perkins and Cruz, 1927).

The structure of the most common and typical unsaturated fatty acid, oleic acid, has been established by several methods ; it is



Evidently, however, different oleic acids could arise by the ethylenic linkage —CH=CH— occupying a different position in the carbon chain, and when two or more such linkages are present the number of possible structures is seen to multiply rapidly.

Moreover, the $\Delta^{9:10}$ -oleic acid (numbering the carbon atoms as shown in the above formula) can itself exist in two forms, each of which is in fact known :



(These structures were formerly invariably assigned in the reverse manner, but recent work from various standpoints has led to the adoption of the configurations here shown.)

A substance containing an ethylenic linkage is under constraint in that the carbon atoms concerned in the "double bond" cannot be supposed to be capable of free rotation ; so that the groups attached to these atoms, instead of being capable of assuming any position in space round them, will tend to take up either of two general arrangements : either with both groups to one side of the plane joining the two unsaturated carbon atoms, or with one group on either side of the plane.

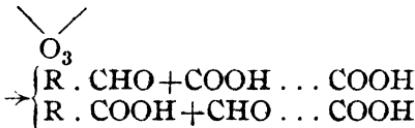
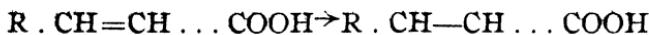
In general two definite and distinct forms of such compounds are, in fact, capable of existence ; that in which the groups are known to be on the same side of the plane joining the unsaturated atoms is termed the *cis*-form, and the other, which is the more stable form and almost invariably has the higher melting point, is known as the *trans*-form.

The more stable, *trans*-isomerides of the higher unsaturated fatty acids have not yet been found to occur in nature, but the natural *cis*-acids can be partially converted to the stable form by treatment with oxides of nitrogen or by heating under pressure with an aqueous solution of sulphurous acid.

The transposition is known as the *elaidin* reaction, and the actual *trans*-isomeride of oleic acid is termed elaidic acid. The equilibrium mixtures of oleic and elaidic acids, or of their esters, or of other higher mono-ethenoid acids which have been examined, each contain about 66 per cent. of the *trans*-(*elaidic*) form, and are approachable from either the *cis*- or the *trans*-compounds (Griffiths and Hilditch, 1932).

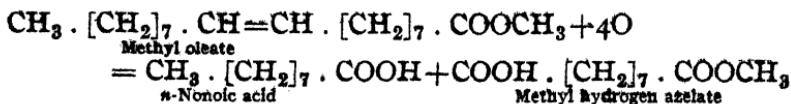
The location of the position of the ethylenic linkage in the carbon chain has been best effected by methods of oxidation, of which three may be briefly mentioned :

(i) Harries showed that ozone is absorbed by an ethylenic linkage, yielding an organic peroxide which on treatment with dilute acid breaks down into a mixture of aldehydes or aldehydes and acids :



This method has proved of considerable value, although resinous products are formed, sometimes to a considerable extent, during ozonization, and in consequence the results are sometimes more qualitative than quantitative in character.

(ii) If the methyl or ethyl esters of unsaturated fatty acids are dissolved in acetone or glacial acetic acid and treated with powdered potassium permanganate at about 60–80° C. until no further action takes place, the following interaction proceeds to the extent of 80–90 per cent. of theory :

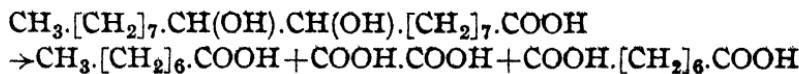


E. F. Armstrong and Hilditch have shown that, by saponification of the acidic oxidation products and subsequent separation, it is usually possible to effect almost quantitative separation of the monobasic and dibasic acids emanating from an individual monoethylenic acid ester. Identification of the scission products leads of course directly to the location of the position of the original ethylenic linkage.

(iii) When the unsaturated fatty acids are subjected to very mild, controlled oxidation a hydroxyl group is added to each unsaturated carbon atom and there result (in variable yields) the corresponding di-, tetra-, hexa-, etc., hydroxy-saturated acids. The oxidation may be carried out either by the action of concentrated hydrogen peroxide in warm acetic acid upon the free acids or their esters or glycerides, or by the rapid action of the calculated amount of dilute permanganate solution upon a very dilute ice-cold solution of the sodium salt in presence of excess of alkali.

The hydroxy-saturated acids are frequently produced in stereoisomeric forms, thus oleic acid yields a 9, 10-dihydroxy-stearic acid, m.p. 132°, with alkali permanganate, and a 9, 10-dihydroxystearic acid, m.p. 95°, when hydrogen peroxide in acetic acid solution is the oxidant.

Either acid, however, is further oxidized almost quantitatively into *n*-octoic acid, oxalic acid and suberic acid when treated in ice-cold dilute aqueous alkaline solution with a small quantity of potassium permanganate, also in dilute ice-cold solution :



This method is due to Lapworth and Mottram, and it is reasonable to hope that the application of methods (ii) and (iii) will lead to more rapid elucidation of the structure of the unsaturated fatty acids than has hitherto obtained.

The structure of the polyethylenic acids has also received considerable attention, but in many cases the evidence is not conclusive when more than three double bonds are

present in the fatty acid molecule. The constitutions of the diethenoid linoleic acid and the triethenoid linolenic acid have been satisfactorily settled by oxidation, but in these and other polyethenoid acids the number of possible geometrical isomerides becomes large, and stereochemical configuration of the natural acids has not always been definitely settled. In certain vegetable seed fats triethenoid acids are present in which all the unsaturated groups are adjacent, or conjugated, and the constitution of these acids is also now fairly well known. In addition to elæostearic acid ($\Delta^{9:10, 11:12, 18:14}$ -octadecatrienoic acid), which is the most important constituent of China wood or tung oil, stereoisomeric forms of this acid have been reported in some other fats, whilst again the occurrence of 4-keto-elæostearic (licanic) acid and of a $\Delta^{9:10, 11:12, 13:14, 15:16}$ -octadecatetraenoic acid has been established in certain other specific seed fats.

The polyethylenic acids, mainly of the C₂₀ and C₂₂ series, which are present in many fish oils have given much more trouble from the point of view of constitution determination. The primary difficulty here is to find a suitable method of separation of the individual unsaturated acids from each other. Fractional distillation of their esters, which will separate one homologue from the next, does not serve to separate esters of acids of the same carbon content which differ in their degree of unsaturation. Moreover, the acids in question, which normally contain 5 or 6 double bonds, are unstable at the temperatures necessary for the distillation of their esters, the unsaturated systems present partly isomerising (probably to cyclic compounds) with the loss of a double bond. The method of evaporative or "molecular" distillation has recently been applied to these esters with some success, but the products obtained by disruptive oxidation of 5 or 6 double bonds do not usually give definite evidence of the position of these bonds in the long aliphatic chain.

The unsaturated fatty acids and their esters readily unite with halogens to give substituted saturated fatty acids. The monoethylenic acids yield liquid dibromo-

addition products, the diethylenic acids (*e.g.* linoleic acids) may give either liquid or crystalline tetrabromo-derivatives, whilst the triethylenic (*e.g.* linolenic) and still less saturated acids lead to hexabromo- or polybromo-derivatives, some of which are solid and progressively less soluble in various solvents.

Linoleic acid from linseed oil, soya bean oil, and other vegetable fats gives a mixture of crystalline and liquid tetrabromostearic acids which was formerly held to imply a corresponding mixture of stereoisomeric acids ("α-" and "β"-linoleic acids). It is generally agreed at the present time that the natural linoleic acid is almost certainly confined to one form, *cis*-Δ^{9:10}-*cis*-Δ^{12:13}-octadecadienoic acid. The production of two or more bromo-addition products, the course of debromination of these products by zinc (when the double bonds reappear in their original Δ^{9:10} and Δ^{12:13} positions), and the mixture of tetrahydroxy-stearic acids produced by alkaline permanganate oxidation of natural linoleic acid or the various stereoisomeric forms into which it has been converted, are now considered to be the result of stereoisomeric changes which accompany the addition or removal of halogen, or the oxidation, as the case may be.

This chapter may be concluded by reference to some of the more important unsaturated natural fatty acids, together with some indication of the nomenclature adopted in dealing with this group.

Nomenclature.—The common acids of the natural fats have received distinctive names such as palmitic, lauric, oleic, etc., which have no chemical significance. The systematic or Geneva method is, however, coming into general use, the saturated acids being distinguished by the suffix *-oic* or *-anoic*, and the total number of carbon atoms being indicated by Greek prefixes. Thus capric acid, C₁₀H₂₀O₂, is *n*-decoic or *n*-decanoic acid; *n*-arachidic acid, C₂₀H₄₀O₂, is eicosoic or eicosanoic acid, etc.

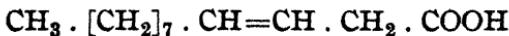
The generic suffix for the ethylenic acids is *-enoic*, so that ordinary oleic acid is Δ^{9:10}-octadecenoic acid, and

erucic acid $C_{22}H_{42}O_2$ is $\Delta^{13:14}$ -docosenoic acid. Although it is still convenient to refer to many of the natural acids by their familiar names (*e.g.*, oleic, erucic, linoleic, linolenic, elæostearic, etc.), it becomes increasingly desirable to use the systematic nomenclature for numerous new acids which have been reported. Even when the position of the unsaturated linkings has not been determined, it is sometimes easier to define an acid by its systematic name, rather than to christen it by some title having reference to the source in which it was first observed. The latter method is perhaps more natural and sometimes the only one available, but with increasing numbers of these rarer acids it places a progressive strain on the memory. Again, it is now recognized that the octadecadienoic acids of fish fats and most animal fats are not identical with the ordinary form of this acid which occurs in the vegetable kingdom, so that it is desirable to confine the term "linoleic acid" to the latter and to refer to other forms as "octadecadienoic acids."

Monoethylenic Acids.—Unsaturated acids occur corresponding with the more typical saturated members from C_{10} upwards, and are the more abundant, and also the more unsaturated, as the carbon content increases up to 22 atoms.

$\Delta^{9:10}$ -Decenoic acid, $C_{10}H_{18}O_2$, occurs in very small proportions in butter fat (together with slightly greater amounts of the $\Delta^{9:10}$ -do-, tetra-, and hexa-decenoic acids mentioned below). Its presence in milk fat was discovered by Smedley in 1912, and confirmed in 1922 by Grün and Wirth, who determined its constitution.

A dodecenoic or lauroleic acid, $C_{12}H_{22}O_2$, occurs to the extent of about 6 per cent. in the head oil of the sperm whale and its constitution may possibly be



Two tetradecenoic or myristoleic acids, $C_{14}H_{26}O_2$, have been recognized at present: one of them forms about 15 per cent. of the acids of sperm head oil, and was shown by Tsujimoto to be the $\Delta^{5:6}$ -acid, whilst the other, which is present to the extent of less than 5 per cent. in sperm

blubber oil and ordinary whale and fish oils, is undoubtedly of the structure $\text{CH}_3 \cdot [\text{CH}_2]_3 \cdot \text{CH}=\text{CH} \cdot [\text{CH}_2]_7 \cdot \text{COOH}$; this acid also forms about 25 per cent. of the acids of Kombo fat (belonging to the Myristicaceæ) but has not yet been observed in quantity in any other instance.

$\Delta^{9:10}$ -*Hexadecenoic* (or *palmitoleic*) *acid*, $\text{C}_{16}\text{H}_{30}\text{O}_2$, occurs in fair quantity in all whale and fish oils, including codliver oil. Its structure has been found to be $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH}=\text{CH} \cdot [\text{CH}_2]_7 \cdot \text{COOH}$ by Armstrong and Hilditch. This acid is now known to occur in nearly all natural fats, in many cases however in very minor quantities.

Octadecenoic or Oleic Acids.—Several natural oleic acids, with the ethylenic linkage in different positions, have been reported to occur naturally, but at present only three are definitely known to exist:—

Ordinary oleic acid whose structure is established quite definitely as $\text{CH}_3 \cdot [\text{CH}_2]_7 \cdot \text{CH}=\text{CH} \cdot [\text{CH}_2]_7 \cdot \text{COOH}$, is by far the most abundant and is found, often in very large proportions, in all natural fats.

Another acid, *petroselinic acid* of parsley-seed oil, is $\Delta^{6:7}$ -*octadecenoic* acid, $\text{CH}_3 \cdot [\text{CH}_2]_{10} \cdot \text{CH}=\text{CH} \cdot [\text{CH}_2]_4 \cdot \text{COOH}$.

Bertram isolated *vaccenic acid* from ox and sheep tallow and gave its structure as $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH}=\text{CH} \cdot [\text{CH}_2]_9 \cdot \text{COOH}$, $\Delta^{11:12}$ -*octadecenoic acid*.

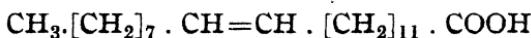
Furthermore, ordinary $\Delta^{9:10}$ -oleic acid, when distilled or treated with sulphuric acid in technical practice or when hydrogenated, suffers migration of the double bond to some extent, together with stereoisomeric change; some of the isomeric oleic acids thus formed, including any elaidic acid, are solid at the ordinary temperature and such acids are known generically as *iso-oleic acids*. The positions to which the double bond has wandered are adjacent to the original, i.e., *cis*- and *trans*- $\Delta^{8:9}$ - and $\Delta^{10:11}$ -octadecenoic acids (Steger and van Loon).

$\Delta^{2:3}$ -*octadecenoic acid*, $\text{CH}_3 \cdot [\text{CH}_2]_{14} \cdot \text{CH}=\text{CH} \cdot \text{COOH}$, has been prepared synthetically from 2-bromo-stearic acid and characterized by Lé Sueur.

An *eicosenoic acid*, *gadoleic acid*, $C_{20}H_{38}O_2$, occurs in moderate amount in whale, fish and fish liver oils; it is the $\Delta^{11:12}$ -acid.

$\Delta^{13:14}$ -*Docosenoic acid*, *erucic acid*, is especially characteristic of oils from seeds of the Cruciferæ. Rape oils contain about 40 per cent. of glycerides of erucic acid and form a convenient source of the acid, which has accordingly been isolated and better characterized than any unsaturated acid other than ordinary oleic acid.

Erucic acid is a solid acid, m.p. $33-34^\circ C.$, and on treatment with nitrogen oxides passes into the corresponding *trans*-isomeride, *brassidic acid*, m.p. 65° . Its structure has been proved by oxidation to be



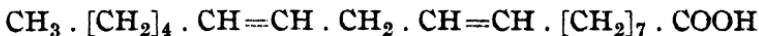
$\Delta^{11:12}$ -*Docosenoic acid*, *cetoleic acid*, is present in many marine animal oils, usually in small quantities.

$\Delta^{15:16}$ -*Tetracosenoic acid*, *selacholeic or nervonic acid*, occurs in the liver oils of some Elasmobranch fish and also in brain cerebrosides.

More Highly Unsaturated Acids.—These fall into two groups :

(i) *Acids of the C₁₈ Series.*—Linoleic and linolenic acids form a distinctive and widespread group characteristic of the “drying” and “semi-drying” vegetable oils.

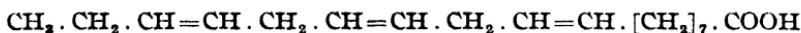
Linoleic acid, as already stated, is considered to be *cis*- $\Delta^{9:10}$ -*cis*- $\Delta^{12:13}$ -octadecadienoic acid :



On addition of bromine it yields about equal parts of a crystalline tetrabromostearic acid (m.p. 114°) and of a liquid form of this acid, the crystalline variety being insoluble in petroleum ether. On oxidation with dilute cold alkaline permanganate solution it yields a certain amount (about 50 per cent. of theory) of two tetrahydroxystearic acids, which melt at 157° and 173° . On isomerization (elaidinization) linoleic acid gives a crystalline isomer (m.p. $28-29^\circ$)

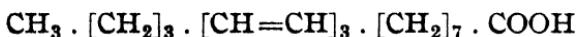
which on oxidation gives two more tetrahydroxystearic acids, m.p. 122° and 146°.

Linolenic acid may well, by analogy with linoleic acid, be *cis*-Δ^{9:10}-*cis*-Δ^{12:13}-*cis*-Δ^{15:16}-octadecatrienoic acid :



Like linoleic acid, it yields a mixture of bromo-addition products (hexabromostearic acids) of which one is a crystalline compound (m.p. 181°) insoluble in ether, the remainder being liquid or gummy and freely soluble in ether. Two hexahydroxystearic acids have been obtained in comparatively small yield when linolenic acid is oxidized with alkaline permanganate. They melt at 173–175° and 203°.

Elæostearic acid, Δ^{9:10}, 11:12, 13:14-octadecatrienoic acid, contains three conjugated double bonds, and its glycerides, present in quantity in tung oil, have the property of polymerizing to a gelatinous form when heated to about 290° C. The presence of the conjugated system causes the addition of iodine halide to be restricted when the iodine value is determined by means of Wijs or similar reagents, but the amount of hydrogen taken up by the acid on hydrogenation corresponds with the presence of three double bonds, whilst the isolation of azelaic and *n*-valeric acids from its products of oxidation shows that the acid has a structure

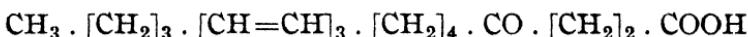


The natural or “ α ”-elæostearic acid, m.p. 49°, is transformed by the action of light into a higher melting isomeric form, m.p. 71° (“ β ”-elæostearic acid). The products formed by union of both forms of the acid with atmospheric oxygen on the one hand, and with maleic anhydride on the other, have been studied in considerable detail by Morrell and co-workers, who have suggested that the difference between the α and β acids lies in different configurations (e.g. *cis-cis-trans-* and *trans-cis-cis*-) of the ethylenic groups.

An instance, at present unique, of a tetra-ethenoid C₁₈

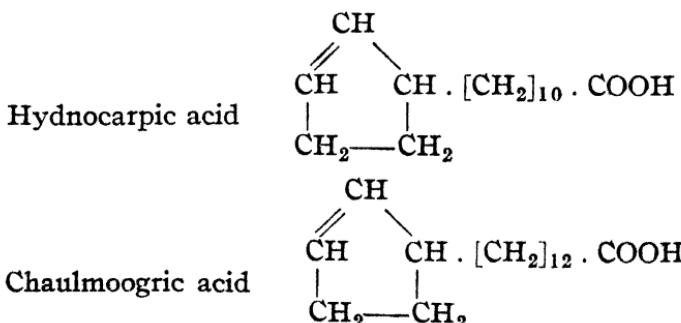
acid is that present in the seed fat of *Parinarium laurinum*; the four double bonds are conjugated and the structure of the acid is $\text{CH}_3 \cdot \text{CH}_2 \cdot [\text{CH}=\text{CH}]_4 \cdot [\text{CH}_2]_7 \cdot \text{COOH}$ ($\Delta^{9:10}$, $11:12$, $13:14$, $15:16$ -octadecatetraenoic acid).

4-Keto- $\Delta^{9:10}$, $11:12$, $13:14$ -octadecatrienoic (licanic) acid is present in quantity in the glycerides of oiticica oil and a few other tropical fats. It was at first believed to be an isomeric form of elæostearic acid, but was later shown to contain a keto-group, its constitution being established as



An acid isomeric with linoleic acid, $\text{C}_{18}\text{H}_{32}\text{O}_2$, but containing only one unsaturated residue (an acetylenic linkage — $\text{C}\equiv\text{C}$) is known as *tariric* acid. It is of rare occurrence but deserves mention on account of the unusual presence of an acetylenic residue in a natural fatty acid; it is a $\Delta^{6:7}$ -octadecenoic acid, and is thus the analogue of the ethylenic petroselinic acid (p. 19).

Similarly, *chaulmoogric acid*, $\text{C}_{18}\text{H}_{32}\text{O}_2$, and *hydnocarpic acid*, $\text{C}_{16}\text{H}_{28}\text{O}_2$, are of the same general formula $\text{C}_n\text{H}_{2n-4}\text{O}_2$ as the linoleic acids, but contain only one ethylenic linkage, the absence of other two hydrogen atoms being occasioned by the presence of a closed carbon ring-system:



Gorlic acid is an analogue of chaulmoogric acid, with a double bond in the aliphatic chain as well as in the cyclopentene ring.

The glycerides of these acids have only been found so far

in chaulmoogra and similar oils of the genera *Taraktogenos* and *Hydnocarpus*.

(ii) *Acids of the C₂₀ and C₂₂ Series.*—Glycerides of very highly unsaturated acids containing 20 and 22 carbon atoms and four, five, or even six ethylenic linkages (as indicated by iodine absorption) are found in quantity in marine animal oils, and especially in fish liver oils. There is some indication that much smaller amounts of the same acids, and perhaps also of similarly unsaturated C₁₈ acids, are present in the livers of many animals.

These acids (at one time termed "clupanodonic acid" and believed to be C₁₈H₂₈O₂) are now known to be members of the C₂₀ and C₂₂ series, and may include acids of the formulæ C₂₀H₃₀O₂, C₂₀H₃₂O₂, C₂₂H₃₂O₂, and C₂₂H₃₄O₂. They absorb oxygen and also polymerize to resinous bodies with extreme ease. Tsujimoto obtained by ozonization of "clupanodonic acid" a yield of nearly 50 per cent. of succinic acid, which indicated that a considerable proportion of groupings of the nature =C . [CH₂]₂ . C= was present in the molecule, and also that unsaturation must commence at the third or fourth carbon atom from the carboxyl group. Toyama and Tsuchiya carried out many similar studies of the constitution of various of these polyethenoid acids, isolated by means of high vacuum distillation of their esters, and suggested that C₂₀ tetra- and penta-ethenoid acids, and C₂₂ penta- and hexa-ethenoid acids were present; they assigned structures based on their oxidation data to a number of these supposed acids, a typical example being Δ_{4:5}, 8:9, 12:13, 15:16, 18:19-eicosapentaenoic acid (C₂₀H₃₀O₂). Farmer and van den Heuvel separated the various homologous groups of the esters of cod liver oil unsaturated acids by means of evaporative distillation in the molecular still (the temperature of the esters never exceeding 120°) and found that the C₂₀ acids contained an average number of 4·9 double bonds per molecule, and the C₂₂ acids an average of exactly six double bonds per molecule; they showed that the acid C₂₂H₃₂O₂ was structurally homogeneous, non-conjugated, and yielded n-behenic acid on hydrogenation,

and from its oxidation products they concluded that the molecule contained as terminal groups $\text{CH}_3 \cdot \text{CH} =$ and $=\text{CH} \cdot [\text{CH}_2]_2 \cdot \text{COOH}$, the remainder of the molecule being made up of four $=\text{CH} \cdot \text{CH}_2 \cdot \text{CH} =$ groups and one $=\text{CH} \cdot [\text{CH}_2]_2 \cdot \text{CH} =$ group.

It is thus now clear that in the vegetable unsaturated acids unsaturation nearly always commences at the $\Delta^{9:10}$ position, whereas in the marine animal C_{20} and C_{22} acids it usually commences at the $\Delta^{4:5}$ position. Again the grouping $=\text{CH} \cdot \text{CH}_2 \cdot \text{CH} =$ is frequent both in the vegetable and the marine animal polyethenoid acids but another, which is extremely rare in the vegetable fatty acids, is also prominent in the marine animal group, namely, $=\text{CH} \cdot [\text{CH}_2]_2 \cdot \text{CH} =$.

The Japanese investigators have also reported the presence, in marine animal oils, of a triethenoid C_{16} acid and of hexaethenoid C_{24} and C_{26} acids.

The table on p. 25 gives the melting- and boiling-points of the acids described above and of their methyl esters, together with the melting-points of their fully brominated addition products and of the corresponding hydroxylated saturated acids obtained by gentle oxidation (*cf.* oleic acid, p. 15), where these are available.

Unsaturated Hydroxy-acid. Ricinoleic Acid.—Hydroxylated fatty acids are probably quite widely distributed in nature, various individuals having been described as being present, usually in small quantities, in the rarer fats and in many waxes.

The only member of the group which need be mentioned here is ricinoleic acid,

$\text{CH}_3 \cdot [\text{CH}_2]_6 \cdot \text{CH(OH)} \cdot \text{CH}_2 \cdot \text{CH}=\text{CH} \cdot [\text{CH}_2]_7 \cdot \text{COOH}$,
the triglyceride of which is the main constituent of castor oil, which is exceptional in being composed almost exclusively of a hydroxylated glyceride.

The acid is a thick oil at ordinary temperatures and melts at $4-5^\circ \text{ C.}$; when heated, even under reduced pressure, it polymerizes or is converted into internal

Acid.	Formula.	M. point.	B. point.	M. point.	B. point.	Methyl ester.		No. of added Br. or (OH).	Bromo- and hydroxy-derivatives.
						Bromo-acid m. point.	Hydroxy acids m. point.		
<i>Monoenylic:</i>									
$\Delta^{9:10}$ -Decenoic ..	$C_{10}H_{18}O_2$	142°/4 mm.	liq.	115-116°/1.2 mm.	2 (Di-)	liq.	liq.		
$\Delta^{9:10}$ -Dodecanoic ..	$C_{12}H_{22}O_2$	liq.	liq.	89-90°/1 mm.	"	liq.	liq.		
$\Delta^{9:10}$ -Tetradecenoic ..	$C_{14}H_{26}O_2$	liq.	liq.	110-111°/1 mm.	"	liq.	liq.		
$\Delta^{9:10}$ -Tetradecenoic ..	$C_{14}H_{26}O_2$	liq.	liq.	108-109°/1 mm.	"	liq.	liq.		
$\Delta^{9:10}$ -Hexadecenoic ..	$C_{16}H_{30}O_2$	"	"	134-135°/1 mm.	"	liq.	liq.		
$\Delta^{9:10}$ -Oleic ..	$C_{16}H_{34}O_2$	16°	"	151-152°/1 mm.	"	liq.	liq.		
$\Delta^{9:10}$ -Elaidic ..	"	44°	"	150°/1 mm.	"	liq.	liq.		
$\Delta^{6:7}$ -Octadecenoic (cis) ..	"	30°	"	150°/1 mm.	"	liq.	liq.		
$\Delta^{6:7}$ -Octadecenoic (trans) ..	"	53°	"	160°/1 mm.	46-47°	liq.	liq.		
Gadoleic ..	$C_{20}H_{38}O_2$	25°	"	169-170°/1 mm.	"	liq.	liq.		
Erucic ..	$C_{22}H_{42}O_2$	33-34°	"	"	"	liq.	liq.		
Cetoleic ..	"	"	"	"	"	liq.	liq.		
<i>Hydroxymonoethylenic:</i>									
Ricinoleic ..	$C_{10}H_{18}O_3$	5°	"	"	"	liq.	liq.		
Ricinoleic ..	"	53°	"	"	"	liq.	liq.		
<i>Monooctylenic:</i>									
Taric ..	$C_{10}H_{18}O_2$	50°	"	"	"	liq.	liq.		
<i>Cyclic Monooctylenic:</i>									
Hydnocarpic ..	$C_{10}H_{28}O$	60°	"	203°/20 mm.	2 (Di-)	liq.	liq.		
Chaulmoogric ..	$C_{18}H_{32}O_2$	68°	248°/20 mm.	22°	227°/20 mm.	"	"		
Linoleic ..	$C_{10}H_{32}O_2$	liq.	228°/14 mm.	liq.	154-155°/1 mm.	4 (Tetra-)	liq., 114°	157°, 173°	
<i>Triethylenic:</i>									
Linolenic ..	$C_{10}H_{30}O_2$	liq.	"	liq.	155°/1 mm.	6 (Hexa-)	liq., 181°	175°, 203°	
Elæostearic ..	"	{49° (a) 71° (b)}	235°/12 mm.	liq.	"	"	141°	"	
<i>Polyethylenic:</i>									
" Clupanodonic "	$\left\{ \begin{array}{l} C_{20}H_{38}O_2 \\ C_{22}H_{42}O_2 \\ C_{24}H_{46}O_2 \\ C_{26}H_{50}O_2 \end{array} \right\}$	liq.	"	liq.	160-165°/1 mm.	8 (Octa-)	above	200°	
"	"	"	"	liq.	170-175°/1 mm.	10 (Deca-)	"	(decom-)	
"	"	"	"	liq.	"	12 (Dodeca-)	"	position)	

anhydrides (estolides) and is also broken down into oenanth-aldehyde, $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CHO}$, and undecylenic acid, $\text{CH}_2=\text{CH} \cdot [\text{CH}_2]_8 \cdot \text{COOH}$, or (as sodium salt) into methyl *n*-hexyl carbinol, $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH(OH)} \cdot \text{CH}_3$, and sebacic acid.

It yields a solid *trans*-isomeride *ricinelaidic* acid, m.p. 54° , on treatment with oxides of nitrogen, and is converted by hydrogenation into *12-hydroxystearic* acid, m.p. 78° .

Gentle oxidation with cold dilute alkaline permanganate produces two 9, 10, 12-trihydroxystearic acids melting at 115° and 142° respectively.

CHAPTER III.—THE MORE NOTABLE ALCOHOLIC CONSTITUENTS OF NATURAL FATS AND WAXES

General.—The number of alcohols which are found combined in fats and waxes is not so great as that of the natural fatty acids. Three distinct types of alcohols exist, the first and most abundant being the trihydric alcohol glycerol, $\text{CH}_2(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2(\text{OH})$, which is the characteristic alcohol present in all fats, in contrast to the waxes. A dihydric alcohol, trimethylene glycol, is formed from glycerol under certain conditions of fermentation of the fats and may be mentioned with glycerol, since it is not infrequently present in the case of rancid or decomposed crude fats, especially if the latter are of animal origin.

The alcohols which cause the waxes to possess their characteristic properties are quite different from glycerol in kind, and are, in fact, the analogues of the higher fatty acids. They range from a molecular content of 12 carbon atoms up to about 30 carbon atoms, and are most frequently fully saturated, although mono- and probably di-ethylenic alcohols containing 16, 18 and 20 carbon atoms in the molecule are present in fair quantity in the oils of the sperm and Arctic sperm whales.

Finally, there are certain alcohols of much more complex and not fully ascertained structure, closely related to the terpene compounds, which are present in greater or less degree in all natural fats and waxes. In most cases the proportion of these is very small—less than 1 per cent. of the total fat—but in certain instances, notably wool fat and some liver oils, the proportion is considerably larger. Some half-dozen of these sterols, as they are termed, have

been definitely characterized and it is found that they fall into two well-defined groups, the zoosterols or cholesterols which are characteristic of all animal fats, and the phytosterols which are equally limited to occurrence only in the fats and waxes of the vegetable kingdom.

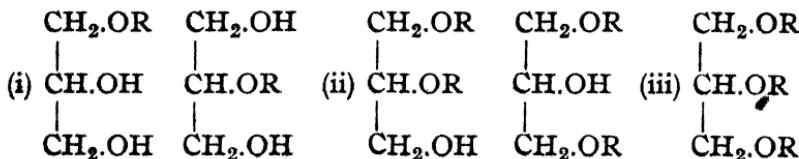
Glycerol and Trimethylene Glycol.—Glycerol is so familiar in the form of the distilled glycerine of the Pharmacopoeia that its properties do not require detailed attention here, whilst its technical production demands consideration later in a separate section of this book.

It is not always appreciated, however, that the pure alcohol is a solid at the ordinary temperature of a cool room, its melting point being 20° C. Glycerol exists extremely readily, however, in the supercooled state, and it is for this reason that solid glycerol is almost unknown. Solidification results when a crystal of glycerol is introduced into cold liquid glycerol, and the resulting solid is made up of large hard crystals which liquefy but slowly at the melting point. Occasionally, in cold weather, glycerine in storage in drums becomes infected with a few crystals of the solid alcohol, and the whole of the contents of the drum may solidify and give rise to some trouble in re-melting.

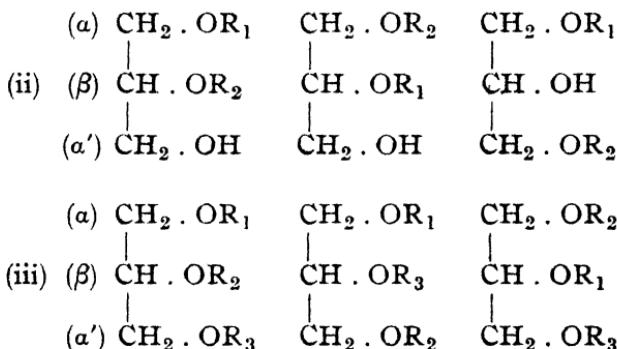
The specific gravity of pure glycerol at 15° (referred to water at the same temperature) is 1.2647, and its refractive index is 1.4758 at 12.5° C. It boils at 290° C. with some decomposition at atmospheric pressure, and unchanged under reduced pressure, e.g. at 220°/100 mm., 210°/50 mm., 182°/20 mm., 167°/10 mm., and 155°/5 mm.

It is exceedingly hygroscopic, miscible with water and with alcohol in all proportions, but less soluble in ether and almost insoluble in light petroleum.

Obviously it can yield mono-, di- or tri-glycerides on esterification :



If each fatty acid residue is different (for example, palmitic, oleic, and stearic) it is obvious that there may be three isomeric diglycerides and three isomeric triglycerides :



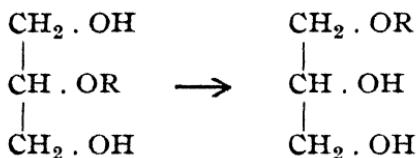
Diglycerides are sometimes found in natural fats, but probably never in freshly-matured, undecayed fats ; whilst monoglycerides are not met with in nature.

Reference is made in Section II., Chapter III., when dealing with the composition of natural fats, to those cases in which the constituents of some of the more common fats are now known with some certainty. It is quite evident that the physical properties of the fats may depend to a considerable extent upon the ultimate composition of the constituent glycerides. A much-quoted instance is the case of cacao butter and mutton tallow, the fatty acids of which are approximately the same :

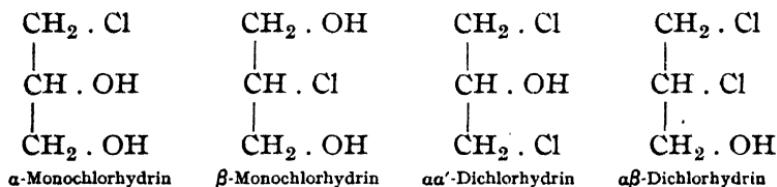
Percentage of :		Cacao butter.	Mutton tallow.
Myristic acid	0	1.5
Palmitic acid	23.2	21.0
Stearic acid	33.6	30.0
Oleic acid	41.8	43.0
Linoleic acid	1.4	5.0

In spite of this similarity of composition, cacao butter, which contains large proportions of oleopalmitostearin and oleodistearin, is a hard, almost waxy fat with a brittle fracture and comparatively low melting point (34°), whereas mutton tallow, with a high melting point ($44\text{--}49^\circ$), is greasy to the feel and does not fracture cleanly.

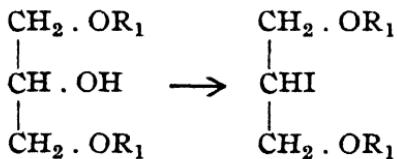
It might be thought that the problem of glyceride structure could be attacked by synthesis, step by step, of various glycerides, but unfortunately, as Emil Fischer has shown, an acid group attached to the β -hydroxyl group of glycerol is capable of migrating during chemical interaction to the α -position :



If it were otherwise, synthetic glycerides of known configuration could be prepared from the hydrochloric esters of glycerol (known as chlorhydrins), each of which can be prepared so that its constitution is known :



Thus from the $\alpha\alpha'$ -dichlorhydrin or $\alpha\alpha'$ -diiodohydrin and the silver salt of a fatty acid the corresponding diglyceride and diglyceride-iodohydrin could be prepared :



During subsequent interaction with the silver salt of a second fatty acid, however, migration of the acyl radicals attached to the α - and β -glyceryl hydroxyl groups usually takes place.

E. Fischer and his co-worker Bergmann commenced investigations whereby desired hydroxyl groups of the glycerol could be "protected" from intramolecular change

of this kind, but the work was restricted to simple acids of the type of acetic or benzoic acid.

Later, methods were devised for the synthesis of mixed glycerides in which possibilities of acyl migration were excluded as far as possible. In America, King and collaborators employed Fischer's methods, whilst Malkin and his co-workers at Bristol have devised simpler methods which lead to the same result; in Holland, Verkade has employed the triphenylmethyl group to combine with one of the α -hydroxyl groups in glycerol prior to esterification with fatty acids. Further details of the synthesis of mixed glycerides of known configuration must be consulted in the more comprehensive monographs or in the original literature.

Malkin and collaborators have made exhaustive studies of the melting points and the X-ray spectra of series of both simple and mixed triglycerides. They have shown that simple triglycerides and also α -mono- and $\alpha\alpha'$ -di-glycerides exist in three polymorphic forms, whilst both symmetrical and unsymmetrical mixed triglycerides exist in four forms. The three general modifications are a stable (β) form in which the long carbon chains are inclined with respect to the planes formed by the terminal methyl groups, a less stable monotropic (α) form in which the chains are vertical, and a third form which is not truly crystalline but vitreous (glass); the fourth form referred to in the mixed triglycerides is known as the β' form, lies in stability between the α and β forms, and, like the β forms, possesses an inclined carbon chain.

Our knowledge of the synthetic mixed triglycerides is still mainly restricted to compounds in which all three acyl radicals are those of saturated acids. Although the information now available is beginning to be of considerable assistance in deciding the configuration of some of the mixed glycerides which occur in natural fats, this aspect of natural glyceride structure has up to the present not been developed to any large extent.

Trimethyleneglycol, $\text{CH}_2(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2(\text{OH})$, is a

product of fermentative decay of fats occasionally met with in crude oils which have developed a high free fatty acid content. It is a liquid, resembling glycerol in viscosity, solubility in water, and to some extent in hygroscopic nature, but boils at a lower temperature ($210\text{--}211^\circ$).

It is important technically because its presence cannot be tolerated in glycerine which is destined for nitration and use in explosives, and therefore it is important to ensure that it does not enter into the glycerine fractions which are collected as dynamite glycerine during fractional distillation.

The Aliphatic Wax Alcohols.—These consist of straight-chain compounds which are the exact analogues of palmitic, stearic, oleic (linoleic), *n*-arachidic, and other acids.

Some properties of the more common members of this group which have been definitely shown to be chemical individuals are given in the next table :

Alcohol.	Formula.	M.p.	B.p.	Other details.
<i>Saturated</i> —				
Hexadecyl (cetyl) alcohol ..	$C_{16}H_{33} \cdot OH$	50°	151°/2 mm.	Acetate, m.p. 23°
Octadecyl alcohol ..	$C_{18}H_{37} \cdot OH$	59°		m.p. 31°
Eicosyl alcohol ..	$C_{20}H_{41} \cdot OH$	71°		" 44°
Hexacosyl alcohol ..	$C_{26}H_{53} \cdot OH$	79.5°		" 65°
Triacontanyl alcohol ..	$C_{30}H_{61} \cdot OH$	86.5°		" 75°

Alcohol.	Formula.	M.p.	B.p.
<i>Unsaturated</i> —			
Hexadecenyl alcohol ..	$C_{16}H_{31} \cdot OH$	liquid	153°/2 mm.
Octadecenyl alcohols ..	$C_{18}H_{35} \cdot OH$	"	
Eicosenyl alcohols ..	$C_{20}H_{39} \cdot OH$	"	

The complete series of all the saturated alcohols up to *n*-pentatriacontanyl alcohol ($C_{35}H_{71} \cdot OH$) has been synthesized by reduction of the esters of the normal fatty acids containing the same number of carbon atoms. The

naturally occurring alcohols from $C_{26}H_{53}(OH)$ to about $C_{34}H_{69}(OH)$, found in various plant and insect waxes, are almost invariably almost inseparable mixtures of two, three or more homologues with even numbers of carbon atoms. Chibnall, Piper *et al.* have recommended that the names ceryl, melissyl, etc., alcohols which refer to products from natural sources should be abandoned in so far as they are intended to refer to definite molecular species such as $C_{26}H_{53}(OH)$, $C_{30}H_{61}(OH)$, etc.

The saturated and unsaturated alcohols containing 16, 18, and 20 carbon atoms per molecule are the main alcoholic constituents which replace glycerol in sperm and Arctic sperm whale oils. Solid esters of cetyl alcohol with lauric, myristic and palmitic acids occur in the head oil of the sperm whale, and are left as a residue when the semi-solid crude oil is submitted to pressure. If, however, the sperm head and blubber oils are regarded as a whole, it will be found that the alcohols of 18-carbon atom content are more prominent than cetyl alcohol. Some proportion of these alcohols consists of the saturated *n*-octadecyl alcohol which melts at 59° , although most of the C_{18} alcohols present are unsaturated, and probably contain a small proportion of a diethylenic alcohol $C_{18}H_{33}(OH)$. The monoethylenic alcohols $C_{18}H_{35}(OH)$ possibly occur in isomeric forms, of which one corresponds with oleic acid and has the formula $CH_3 \cdot [CH_2]_7 \cdot CH=CH.[CH_2]_7 \cdot CH_2(OH)$.

A minor proportion of the C_{16} alcohols is also unsaturated, probably the monoethylenic compound $C_{16}H_{31}(OH)$.

The C_{20} alcohols are not present in so great an amount as the C_{16} and C_{18} compounds and are unsaturated (mono- and di-ethylenic).

All the foregoing unsaturated alcohols are readily converted by hydrogenation into the saturated normal alcohols $C_{16}H_{33}(OH)$, $C_{18}H_{37}(OH)$, and $C_{20}H_{41}(OH)$, melting respectively at 50° , 59° , and 71° C.; this, of course, shows that the unsaturated compounds are straight-chain derivatives related to the saturated bodies in the same manner as oleic is to stearic acid.

Whilst the unsaturated members are oily liquids the three saturated alcohols crystallize in large, hard, waxy flakes which exhibit considerable lustre in consequence of high refractivity.

The Sterols.—These compounds constantly accompany fats and waxes whether of vegetable or animal origin, and must receive brief notice here in view of their undoubted biochemical significance, although they are of no present moment in most of the technical applications of the fats and waxes. References to recent work on the constitution of the sterols will be found in the bibliography at the end of this section.

Since the sterols are insoluble in water or alkalies, they appear in the "unsaponifiable" residue of oils and fats, and, indeed, frequently form a considerable proportion of this material. In the original fats the sterols may occur either in the free state or as fatty acid esters.

The free sterols are characterized by their power of forming crystalline additive compounds with the glucoside principle digitonin; the addition products are almost completely insoluble in alcohol and serve as a useful means for the separation and identification of small quantities of sterols. The use of the method on a large scale is restricted in practice by the expensive character and comparative rarity of the reagent digitonin.

Various colour reactions have also from time to time been recommended as characteristic for sterols, but, like most tests of the kind, these are not very reliable, since other compounds (in the present instance various other complex terpene derivatives) also produce similar colour changes. The Liebermann-Burchard reaction, however, may be quoted: The material is dissolved in a small quantity of chloroform and 20 drops of acetic anhydride added, followed by one drop of concentrated sulphuric acid. The presence of any sterol is indicated by the development of a definite tint (*cf.* details below).

It has already been stated that the sterols occurring in animals and plants can be differentiated.

Of the animal or zoosterols, the most abundant is *cholesterol*, $C_{27}H_{45}(OH)$, which is found in abundance in wool fat and to a lesser extent in liver oils and in still smaller quantities in the body, skin, and other fats of all animals, terrestrial and marine. It forms small needle-shaped crystals (from alcohol), m.p. 148.5° C. (with water of hydration). It is optically active, $[\alpha]_D - 35^{\circ}$ in chloroform solution. Cholesteryl acetate melts at $114-115^{\circ}$ ($[\alpha]_D - 42^{\circ}$), and the benzoate at $150-151^{\circ}$ ($[\alpha]_D - 15^{\circ}$). Cholesterol gives a violet to green coloration in the Liebermann-Burchard test.

Other, isomeric zoosterols of the same type are sometimes associated in less amount with cholesterol; of these only the *iso-cholesterol* of wool fat, which melts at 140° and has $[\alpha]_D + 59^{\circ}$ in chloroform (benzoate, m.p. 199° , $[\alpha]_D + 73^{\circ}$), need be mentioned. It gives a green colour with the Liebermann-Burchard reagent.

The corresponding alcohols found in the vegetable kingdom are known as phytosterols, and appear to occur in somewhat greater variety than the zoosterols.

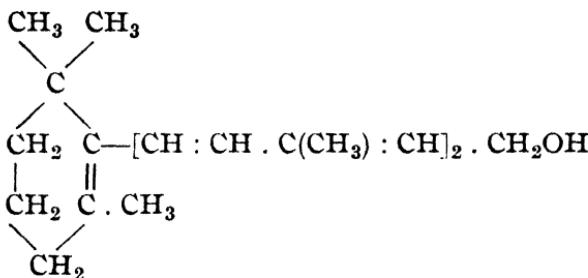
The most widely distributed are the *sitosterols*, $C_{29}H_{49}(OH)$, one of which melts at 139° and has an optical rotatory power $[\alpha]_D - 34^{\circ}$. It crystallizes in tufts of needles, more stumpy than those of cholesterol, and gives a similar coloration to the latter in the Liebermann-Burchard test. Sitosterol acetate melts at 127° , the benzoate at 145° . Sitosterol has been found in the oils from many cereals, maize, cottonseed, peas, beans, and numerous other seeds.

Phytosterols isomeric or homologous with sitosterol have also been described by various workers.

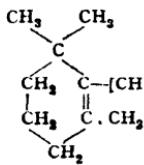
Vitamins A and D.—These fat-soluble vitamins are present in the unsaponifiable matter of many fats, especially in animal liver oils, notably fish liver oils such as those of cod or halibut.

Vitamin D probably exists in several forms which are triethylenic alcohols belonging to the sterol group. One form is produced when the natural triethylenic sterol ergosterol is exposed to ultra-violet light.

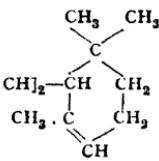
Vitamin A is an unsaturated alcohol of the formula



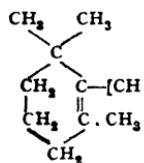
which is closely related to the three isomeric α , β and γ carotenes, especially to β -carotene.



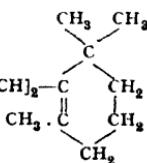
α -Carotene.



α -Carotene.



β -Carotene.



This hydrocarbon can be converted under suitable conditions in the animal organism into vitamin A. Vitamin A occurs to some extent in the free condition in liver fats and other animal organ fats, but it is probable that to a larger degree it occurs in combination with most of the fatty acids which are present in the fat in question in the form of glycerides.

CHAPTER IV.—METHODS OF ANALYSIS AND IDENTIFICATION EMPLOYED FOR FATS AND WAXES

Introductory.—The wide variety of applications of fats and waxes and the equally wide variations in the nature of these raw materials, coupled with the impracticability of their rapid separation into their ultimate individual components, has led to the elaboration of a very great number of largely empirical but reasonably accurate and carefully worked out quantitative tests.

These methods, many of which have been carefully standardized, are of fundamental importance to the analyst who is called upon to assess the values of fatty products, especially in the many cases where a given fatty constituent is liable to adulteration or substitution by others. In consequence the literature dealing with the technological analysis of fats and waxes and their products is enormous in extent, and the whole subject forms an important branch of analytical chemistry. A comprehensive discussion of the analysis of oils, fats, and waxes requires a volume to itself and, indeed, a number of manuals have been published which deal with this subject in its broadest aspects. Reference is made to some of these works in the sectional bibliography (p. 95), and one or other of them should be consulted when more complicated analytical problems, requiring more specific treatment than the methods described in this chapter afford, present themselves. It may be added here that of late years many of these analytical methods have been scrutinized or re-standardized by committees set up by various scientific societies, and there has come into existence a large number of reports by these committees on

one or other analytical method. Attention should be drawn especially to reports published in the *Analyst* from time to time by the Analytical Methods Committee of the Society of Public Analysts, and to numerous specific reports contributed by committees of the American Oil Chemists' Society in this field (published in the U.S. journals *Oil and Fat Industries* (1924-1931), and *Oil and Soap* (1932 onwards)).

Apart from isolated methods of analysis peculiar to certain products or industries, however, the chemist engaged in the majority of the industries in which fats and waxes are utilized relies mainly upon a relatively small number of physical and chemical methods by which to assess the properties of the materials with which he is dealing.

The principles upon which these methods are based and a very brief description in each case of the manipulative details essential to accurate results will therefore be given, and it will be found that the analytical processes described cover the greater part of the technological fat-chemist's needs, as distinct from the more exacting tests required in many cases by public or consulting analysts who are concerned with rigorous degrees of purity or the possible presence of small quantities of adulterants in the final fatty products sold in commerce.

It is the custom in most treatises to deal first with the physical and then with the chemical methods of analysis, but this order is reversed here because the quantitative tests which are most widely required and most fundamental to the industries of fats and waxes are undoubtedly the *saponification value*, which indicates to some extent the average molecular complexity of the material, and the *iodine absorption*, which is a reliable index of the relative proportion of unsaturated (or, as a general rule, liquid) components.

The chemical criteria of fats and waxes, formerly known as "constants," have been classified in two divisions by Lewkowitsch: *characteristics* and *variables*. Whilst the values concerned cannot be always assigned strictly to one

or other of these classes, yet the distinction should be borne in mind. No analytical value of the natural fats or waxes is rigidly constant, yet in many cases well-defined values exist which may vary within relatively narrow limits ; such values are termed *characteristics*. Alternatively, there are other figures which alter quite fortuitously, the varying free fatty acidity of one and the same kind of fat being a common example : values of this kind are termed *variables*. Obviously, the same property may, according to circumstances, fall within either category : thus the acetyl value of castor oil, which is almost exclusively composed of the glyceride of a hydroxy-fatty acid, is a *characteristic* of this fat, whereas for the greater majority of fats and waxes the acetyl value is a *variable*, indicating the adventitious presence of irregular amounts of alcoholic or hydroxylic compounds such as mono- or di-glycerides, free fatty alcohols or sterols, etc.

The analytical tests which will be referred to in some detail are as follows :

Chemical Tests.

1. Saponification value—*characteristic* for most fats and waxes, and free fatty acidity or acid value—*variable*.
2. Iodine and thiocyanogen absorption and formation of crystalline bromo-addition products—*characteristic* for unsaturated fats.
3. Proportion of water-soluble or water-insoluble volatile fatty acids present—*characteristic* for fats containing lauric acid and acids of still lower molecular weight.
4. Acetyl value—indicating the proportion of free hydroxylic compounds present.
5. Content of “unsaponifiable” matter—*characteristic* or *variable* for different classes of fats and waxes.
6. Analysis of glycerol.
7. Analysis of rosin.

A few of the more generally useful specific chemical tests, including the thermal effect on treatment with sulphuric acid, and one or two of the better-defined colour reactions of natural fats, are added.

Physical Tests.

1. Setting point and melting point of fats and waxes and of the corresponding fatty acid mixtures contained therein.
2. Specific gravity of fats and waxes.
3. Refractive index of fats and waxes.
4. Viscosity of fats and waxes.

This chapter is concerned with the definition of the meaning of each test and the general indications which each affords as to the nature of the fat or wax under examination, together with a statement of the manipulation and precautions recommended in each case. Numerous examples of the usual range of variation of most of these figures, whether "characteristics" or "variables," will be found if the average analytical data for the various divisions of natural fats and waxes, given in the tables in Section II., Chapter II., are consulted and compared.

CHEMICAL TESTS

i. Saponification Value and Free Fatty Acidity.— Both of these analytical criteria depend, of course, on the same chemical principle, namely, the use of caustic alkali, on the one hand to effect the complete hydrolysis of a glyceride or wax ester, and on the other hand to combine with free fatty acid by neutralization, without saponification of the neutral esters which are usually also present.

There are two systems by which the results of quantitative interaction with caustic alkali have been expressed: (a) as saponification or acid "values" or (b) as saponification equivalents, together with free acidity expressed as a percentage of a definite fatty acid component (most frequently oleic acid).

The *saponification value* is the number of milligrams of KOH required to hydrolyse 1 grm. of the fatty or waxy material; and the *acid value* is the number of milligrams of KOH required exactly to neutralize the free acidity of 1 grm. of the material.

This form of expression has the advantage of being

perfectly general and of requiring no assumption whatever to be made as to the general nature of the material or the specific nature of the free fatty acids present. The data, expressed in these forms, therefore approach to simple numerical indices which are extremely useful to analysts who are largely occupied with the assessment of fats, etc., in foods or other goods, and who by long practice are able to recognize the implications of any variation from the normal in either index. Those engaged in the chemical processing of fats and waxes, however, sometimes find it more convenient to adopt terms of reference which convey, although perforce somewhat approximately, a more direct idea of the actual molecular components which are being dealt with in bulk, and to this end the simple *saponification* and *acid values* are replaced respectively by the *saponification equivalent* and the *percentage of free fatty acid*.

The *saponification equivalent* is the amount of fat or wax saponified by one gram-equivalent of KOH, and is therefore the mean gram-equivalent of the mixture of glycerides or wax esters present in the material examined, *on the assumption that the latter consists exclusively of neutral esters of these types.*

With many fats and some waxes used in technical practice, containing, for example, not more than 2 or 3 per cent. of free fatty acid and less than 1 per cent. of "un-saponifiable" matter, the latter proviso is approximately satisfied, and the *saponification equivalent*, which is related to the *saponification value* by the formula

$$\text{Saponification equivalent} = \frac{56,100}{\text{Saponification value}}$$

affords a fairly clear indication of the *mean* molecular magnitude of the esters (glycerides or otherwise) which are present.

In the cases of fats or waxes containing very high proportions of unesterified material of an alcoholic or hydro-carbon type (such, for example, as wool grease, montan wax, and several other waxes), the saponification equivalent is

almost meaningless, and it is only when the assumption mentioned is substantially justified that it is of practical utility ; nevertheless, as stated, this assumption is valid as an approximation in very many cases of technical importance, especially in the edible fat and the soap industries.

If, again, it is desired to assess the mean molecular magnitude of the neutral components of the material apart from the free fatty acids, this can be carried out on the basis of the difference between the saponification and acid values ; this figure is sometimes referred to as the *ester value*, but is not widely utilized.

The *percentage of free fatty acid*, calculated as such, implies a knowledge or assumption of the mean molecular weight of the free fatty acids. If this is assumed (*M*), then the *percentage of free fatty acid* present is

$$\text{Acid number} \times \frac{M}{561}$$

The value of *M* may be deduced from the saponification equivalent in the case of a mixture of glycerides containing little or no "un-saponifiable" matter ; or it may be (and more generally is) taken as that of the fatty acid present in greatest amount. In most cases it suffices to calculate the free acidity for technical purposes in terms of oleic acid (equivalent 282), except in special cases such as the nut oils (where lauric acid, equivalent 200, or a mean equivalent of 220 may be substituted), palm oil (free acidity usually calculated to palmitic acid, equivalent 256), or castor oil (ricinoleic acid, equivalent 298).

Determination of Saponification Value or Equivalent.—It is necessary to carry out the hydrolysis in alcoholic solution with excess of alkali of at least semi-normal strength in order to attain complete hydrolysis in a reasonable time, and this introduces the following complications :

- (a) In order to obtain a suitably large titration volume it is necessary to employ from 2 to 5 grms. of the fat or wax.
- (b) A certain amount of brown coloration is often

introduced during the heating of the alcohol with caustic alkali, and it is therefore necessary to use a considerable amount (at least 1 c.c.) of phenolphthalein as indicator ; it is also a good plan to add 1 c.c. of a 0·1 per cent. solution of methylene blue in addition to the phenolphthalein, when the end-point is more sharply distinguished by transition from brownish-purple or bluish-purple to a clear pale or dark green.

(c) The alcoholic alkali is liable to be affected if carbon dioxide has access to it, even in small amount, and therefore a blank determination must always be carried out with each test or group of tests.

Solutions Required.—Accurately standardized normal or semi-normal sulphuric or hydrochloric acid.

Approximately normal or semi-normal alcoholic potash (this should be made up in not too large quantities by solution of pure stick caustic potash in alcohol, the solutions being filtered as soon as made to remove undissolved carbonate and kept as far as possible from access to air).

Neutral alcohol (neutralized exactly to phenolphthalein by alcoholic potash).

Procedure.—The material (2–5 g., according to the approximate value expected) is weighed accurately into a 250–300 c.c. flask and mixed with 30 c.c. of neutral alcohol. Alcoholic potash (50 c.c. of approximately semi-normal or 25 c.c. of approximately normal) is run in from a burette with constant stirring and at a constant rate (*e.g.* 2 minutes in every case). The contents of the flask are gently boiled with occasional thorough shaking for one hour under a reflux water or air condenser (the latter conveniently consisting of a 3 or 4 ft. length of $\frac{1}{4}$ -in. glass tubing).

An exactly similar determination is made concurrently as a “blank,” the fat or wax being omitted.

About 1 c.c. of phenolphthalein solution is now added and the saponified solution and the blank are titrated against standard acid, the difference in the titration volumes giving the amount of alkali consumed in terms of standard acid.

Thus, if w is the weight of fat taken, and v_b and v_w the

number of c.c. of normal acid required to neutralize the blank and the actual solutions after refluxing, we have

$$\text{Saponification value} = \frac{(v_b - v_w) \times 56.1}{w}$$

$$\text{and Saponification equivalent} = \frac{1000w}{v_b - v_w}$$

Determination of Free Fatty Acid.—(a) If considerable amounts of free fatty acid are present, the determination can be carried out at the same time as that of the saponification equivalent by warming the neutral alcohol suspension of the fat until all is liquid and adding the alcoholic potash as a titration in presence of phenolphthalein until an almost permanent pink colour is produced, noting the volume of alkali added and then proceeding to add the remainder of the 25 or 50 c.c. of alkali from the burette.

(b) If the proportion of free fatty acid is small, the volume of alkali required in the foregoing method is too small to afford accurate results, and the following procedure is recommended :

The sample (5-10 g.) is accurately weighed into a 250 c.c. flask and one of the following solvents is added :

- (i) 50 c.c. of neutral alcohol ;
- (ii) 25 c.c. of neutral methyl alcohol and 25 c.c. of toluene ;
- (iii) 25 c.c. of neutral alcohol and 50 c.c. of light petroleum (b.p. about 80° C.).

The solution is freely boiled for not more than two minutes, a few drops of phenolphthalein solution added, and titrated with vigorous shaking against a solution of approximately decinormal alcoholic potash (the exact strength of which is concurrently determined against standard acid) until a semi-permanent pink colour appears.

The methyl alcohol-toluene or alcohol-light petroleum mixtures give somewhat better results than alcohol alone.

If v c.c. of alkali (in terms of normal solutions) are required to neutralize w grams of material,

$$\text{Acid value} = \frac{v \times 56.1}{w}$$

$$\text{Percentage of fatty acid (as oleic acid)} = \frac{v \times 28.2}{w}$$

Although the determination of saponification and acid values appears to be a straightforward one, it will be found that considerable care is needed to obtain accurate results with the alcoholic solutions which it is necessary to employ, and the fat-chemist should practise the process repeatedly until he has satisfied himself that he has mastered the conditions necessary and can obtain reliable results.

2. Iodine and Thiocyanogen Absorption and Formation of Crystalline Bromo-addition Products.— The unsaturated higher aliphatic alcohols and acids of fats and waxes combine additively and quantitatively with iodine under suitable conditions, and the amount of unsaturation present is always measured in terms of the capacity to fix or absorb iodine. The iodine value or percentage iodine absorption is simply the weight of iodine thus fixed by 100 grms. of material.

Various reagents may be used to effect the quantitative addition of halogen to the double bonds present, and in some cases iodine itself is not employed, but bromine, in one form or another, takes its place. The amount of halogen consumed by addition to the unsaturated fat is, however, always estimated by adding aqueous potassium iodide to the solution at the end of the contact with halogen, and titrating the liberated iodine with a standard thiosulphate solution. Whatever the halogen employed, therefore, it is easy and convenient to regard the results in terms of percentage absorption of iodine.

If thiocyanogen, $(\text{CNS})_2$, prepared by the quantitative addition of bromine to a suspension of lead thiocyanate in anhydrous acetic acid, is employed in place of any of the halogen solutions used for iodine value determination, it is found that the thiocyanogen unites quantitatively with any oleic or monoethylenic fatty acid present; on the other hand, it combines with approximately one of the two double

bonds present in linoleic acid, and on the average with somewhat less than two out of the three double bonds of linolenic acid. If a known volume of thiocyanogen solution is employed, that remaining uncombined liberates iodine on shaking with excess of aqueous potassium iodide, which can be titrated in the usual manner with thiosulphate solution. The "thiocyanogen value" so obtained (expressed in terms of percentage absorption of iodine) is thus different from the ordinary iodine value in that it differentiates between oleic, linoleic and linolenic acids. In mixtures of these three acids or of fats containing these three acids, therefore, determination of both the iodine and the thiocyanogen value affords a method for the estimation of each of the three unsaturated acids.

Where only oleic and linoleic acids are known to be present, the iodine value alone is sufficient to determine the amount of each acid, assuming that any saturated acids present can be separately determined; or in the absence of the latter, the iodine and thiocyanogen values of a mixture of saturated, oleic, and linoleic derivatives are sufficient to give the components of the mixture. Similarly, with a mixture of saturated, oleic, linoleic, and linolenic derivatives, determination of the proportion of saturated compounds together with that of the iodine and thiocyanogen values leads to the composition of the mixture. At the present time, however, there is some uncertainty as to the precise thiocyanogen values which should be accepted for pure linoleic and linolenic acids, and the application of the method must remain somewhat uncertain until definite agreement has been reached on this point.

Reverting to the subject of iodine values, it may be mentioned that the term "inner iodine value" has been used on the Continent to denote the iodine value of the unsaturated components or acids of a fat, as distinct from the iodine value of the whole fat or fatty acids. In other words, the "inner iodine value" is the iodine value of the unsaturated acids of a fat, determined on the "liquid" acids obtained after separation of the bulk of the saturated

acids in the form of ether- or alcohol-insoluble lead salts (*cf.* this section, Chapter V., p. 87).

Some of the various types of unsaturated derivatives encountered—mono-, di-, tri-, or poly-ethylenic—can be differentiated qualitatively, but to no great extent quantitatively, by the relative solubility and melting-points of the analogous addition-products which they furnish with bromine, and some notes on the use of these derivatives to this end are added after the iodine and thiocyanogen absorption determinations have been described.

Determination of Iodine Absorption.—It is necessary to ensure that the halogen-addition process is complete within a reasonable time, and to this end the iodine is not used alone, but is combined with a "carrier" which increases its reactivity. Three distinct kinds of solution have been utilized for this purpose, of which the Hanus solution is less widely employed in this country than the others :

Wijs Solution : Iodine monochloride in glacial acetic acid.

Hanus Solution : Iodine monobromide in glacial acetic acid.

Hübl Solution : Iodine-mercuric chloride in alcohol.

Preparation of Wijs Solution.—(i) Iodine trichloride (7.8 g.) and iodine (8.5 g.) are dissolved in warm glacial acetic acid and made up to 1000 c.c. with glacial acetic acid in the cold ; or

(ii) Iodine (13 g.) is dissolved in a litre of glacial acetic acid and pure dry chlorine gas is passed through the solution until its titration number to thiosulphate is exactly doubled ($I_2 + Cl_2 = 2ICl$).

The second method is somewhat cheaper where large quantities of the reagent are required, but the first method is much more rapid and simple to carry out—considerations which as a rule outweigh the extra cost of the iodine trichloride.

Wijs solution is said to keep indefinitely in the dark in well-stoppered bottles, but it is preferable in practice

to use reasonably fresh solutions in order to eliminate any possibility of deterioration by accidental access of water vapour, etc. It is most important that all the reagents and solvents used should be perfectly dry.

When used in a comparatively fresh state and with the precautions indicated, it yields highly accurate results and requires less time for contact with the fat than the Hübl method.

Preparation of Hanus Solution.—This is prepared by dissolving together 13 grms. of iodine and 8 grms. of bromine in a litre of glacial acetic acid.

Preparation of Hübl Solution.—(a) Iodine (25 g.) is dissolved in 500 c.c. of 95 per cent. alcohol;

(b) Mercuric chloride (30 g.) is dissolved in 500 c.c. of 95 per cent. alcohol.

The mercuric chloride solution is filtered if necessary and each solution is stored in the dark until required for use, when the reagent is obtained by taking an equal volume of each solution.

Even when kept separately the solution of iodine in alcohol is not permanently stable, whilst if mixed prior to use the actual Hübl solution of iodine-mercuric chloride in alcohol undergoes slow but progressive change.

The Hübl solution requires much longer contact with the fat or wax than Wijs solution to ensure complete addition of halogen to the unsaturated centres, but otherwise it gives equally good results; indeed, in cases where there is a tendency to substitute halogen for hydrogen as well as to add halogen at ethylenic linkages, the use of Hübl's method is to be preferred over that of Wijs, since the latter is more prone to effect substitution as well as addition.

In the actual determination of iodine absorption the following solutions are required:

Standard (decinormal) sodium thiosulphate.

Potassium iodide solution (10 per cent.), and starch solution.

Chloroform or carbon tetrachloride (pure, dry).

Wijs, Hübl, or Hanus solutions.

The amount of fat or wax taken for the analysis is governed by its supposed state of unsaturation: e.g. 0.1-0.2 grm. of a highly-unsaturated fish oil or linseed oil, about 0.25 grm. of soya bean or cottonseed oil, 0.3-0.4 grm. of olive or palm oil, and 0.5 grm. or more of an almost saturated fat such as coconut oil.

The accurately weighed material is placed in a wide-necked bottle (fitted with a well-ground stopper) and dissolved in 15 c.c. of pure chloroform or carbon tetrachloride; Wijs solution (25 c.c.) (or 15 c.c. of each of the components of the Hübl solution) is added and the bottle well shaken, after inserting the stopper (which may be moistened with a drop of potassium iodide solution), and set aside in the dark for the addition process to proceed to completion. This requires 30-60 minutes for Wijs solution and 8-15 hours for Hübl solution: determinations by the latter method are conveniently left overnight at this stage. In the Wijs process it is advisable to adopt a definite time of contact for fats of given types—for example, 30 minutes for fats of iodine absorption up to 120, and 60 minutes for those of higher absorption.

It has recently been stated by Hoffman and Green that addition of 10 c.c. of a 2½ per cent. solution of mercuric acetate in glacial acetic acid directly after adding the Wijs solution causes the absorption of iodine monochloride to be complete in 3 minutes, and that with this modification the latter time of contact can be safely employed, thus considerably shortening the duration of the analysis.

The weight of fat or wax should be so chosen that at least as much iodine, or more strictly iodine monochloride, remains unchanged as is absorbed.

The solution, when the contact time is complete, is mixed with 15 c.c. of 10 per cent. potassium iodide solution and titrated with the standard thiosulphate solution, using starch as final indicator.

A blank determination is carried out with each batch of iodine absorption tests, in all respects as in the actual analysis except that no fat or wax is present.

If w is the weight of fat or wax, and v_b , v_w are the respective numbers of c.c. of thiosulphate solution (reckoned as decinormal) used in the blank and actual analyses, then

$$\text{percentage iodine absorption} = \frac{(v_b - v_w) \times 1.27}{w}$$

Other methods for the determination of iodine values.—A number of other reagents for the addition of halogen to fatty compounds have been proposed, of which the following have received general approval, in some cases for specific purposes.

Winkler employed a mixture of potassium bromide and potassium bromate in presence of hydrochloric acid, causing the liberation of free bromine. The fat (0.1–0.5 g.) is dissolved in carbon tetrachloride (10 c.c.) and mixed with 25 c.c. of a solution containing 5.57 g. of potassium bromate and 40 g. of potassium bromide per litre. Aqueous hydrochloric acid (10 per cent.; 10 c.c.) is added, the container well shaken and allowed to stand from 2 to 4 hours in the dark. The potassium iodide solution (10 per cent.; 10–15 c.c.) and water (150 c.c.) are then added and the liberated iodine titrated with thiosulphate.

Kaufmann employed a solution of bromine in methyl alcohol containing sodium bromide, the solution being prepared by adding 5.2 c.c. of pure bromine to a litre of a 12–15 per cent. solution of anhydrous sodium bromide in anhydrous methyl alcohol. The fat (0.1–0.5 g.) is dissolved in chloroform (10 c.c.), mixed with the bromine solution (25 c.c.) and left in the dark for 30 minutes to 2 hours; the rest of the determination is the same as in the case of the Wijs method.

Rosenmund and Kuhnhenn have employed pyridine sulphate dibromide as halogenating agent. A N/10 solution of the reagent is prepared by dissolving separately pyridine (8 g.) and concentrated sulphuric acid (10 g.) each in glacial acetic acid (20 c.c.), mixing the two solutions cautiously, adding bromine (8 g.) dissolved in glacial acetic acid (20 c.c.), and diluting the whole with glacial acetic acid to one litre. The details of the analysis follow those given for the Wijs method, except that the contact time required

does not exceed 5 minutes. This method has also been used for the determination of iodine value on the micro scale. It is said to give somewhat lower values with fats than the Wijs or Hanus methods, but on the other hand has been found useful in determining the iodine absorption of sterols and similar unsaturated non-fatty compounds.

Toms has found that exposure of films of small quantities of liquid fatty compounds to bromine vapour results in quantitative addition of bromine to the ethylenic bonds present, even when, as in tung oil and a few other cases, these exist as a conjugated system. A single drop of oil (0.02–0.03 g.) is spread in a thin film on a weighed microscope slide and placed in a wide tube closed at each end with a waxed cork, and containing a boat in which are placed a few drops of bromine. After 20–30 minutes the slide is taken out, and excess of bromine removed, either by heating to 50–60° or by a current of warm air. From the increase in weight of the slide the percentage addition of bromine can be calculated, and this can be converted to the corresponding percentage absorption of iodine. This is clearly a useful micro method.

It should be noted that, with the exception of the Toms method, all the above procedures are quantitatively valid only for fats or fatty acids in which the ethylenic linkings are separated from each other by one or more $-\text{CH}_2-$ groups. Unless an extremely lengthy period of contact is given, the ordinary reagents mentioned above fail to react completely with conjugated systems such as those present in elæostearic acid or glycerides. Indeed, in the case of fats containing the latter compounds, it is now generally recognized that the safest means of determining the unsaturation is by hydrogenating a small quantity of the fat under conditions in which the volume of hydrogen necessary for total saturation can be accurately observed. The "hydrogen value" so obtained can be arithmetically transformed, as required, into the corresponding iodine value.

Determination of thiocyanogen absorption.—This method was first proposed by Kaufmann in 1925. As already

mentioned it is intended to discriminate between oleic, linoleic, and linolenic acids, owing to the circumstances that thiocyanogen reacts with approximately one out of the two double bonds in linoleic compounds, and with somewhat less than two out of the three double bonds in linolenic compounds.

The thiocyanogen reagent is prepared as follows: pure lead thiocyanate is dried for at least a week in a vacuum over phosphorus pentoxide, and glacial acetic acid is refluxed with 15 per cent. of acetic anhydride for 3 hours, cooled, and kept for a few days before use. The dried lead thiocyanate (50 g.) is then suspended in the prepared acetic acid (1000 c.c.), well shaken, and left in the dark for about a week in a well-stoppered bottle before use in the preparation of the actual reagent.

All apparatus and filter paper employed throughout the preparation of the reagent and the determination of thiocyanogen values must be thoroughly dried immediately before use at about 120° for at least an hour.

The actual reagent is freshly prepared, immediately before use in determining thiocyanogen values, by addition of bromine to the suspension of lead thiocyanate in acetic acid, the amount of bromine added being exactly that necessary to liberate thiocyanogen, $(CNS)_2$, and convert the lead present into lead bromide. The strength of the reagent should be about 0.16–0.20 N, and each batch should be filtered and an absolutely clear filtrate obtained. It is desirable to employ an excess of 150–200 per cent. of the reagent above that necessary for addition to the unsaturated fat.

The fat (0.1–0.2 g.; dissolved in 20 c.c. of the prepared acetic acid) is placed in contact with the filtered reagent (20 c.c.) for 24 hours in the dark at about 20° C.; aqueous potassium iodide solution (20 per cent., 20 c.c.) is then added and the mixture titrated with standard thiosulphate solution in the usual way.

The extent of absorption depends not only on the excess of reagent employed, but also on the time of contact and

the temperature of the solution, whilst as stated the presence of traces of moisture interferes seriously with the accuracy of the determination. Great attention must therefore be paid to the conditions of the reaction, and complete agreement has not yet been reached as to the standard conditions to be employed. The results hitherto obtained by this method (in conjunction with iodine values and proportions of saturated compounds) are therefore somewhat uncertain, but it appears that, when agreement has been reached upon the standardisation of the method, and more especially upon the thiocyanogen values to be assigned to pure linoleic and linolenic acids and their derivatives, this procedure will be of great value in analysing mixtures containing oleic, linoleic and linolenic acids or glycerides.

Qualitative and Semi-quantitative Discrimination between Unsaturated Fatty Acids by means of their Bromo-addition Products. — Bromine unites readily with unsaturated glycerides or higher fatty acids, and some of the addition products show the following properties :

—	Solubility of "α-"brominated glycerides or fatty acids in:		Bromo-stearic acids.	M.p.
	Light petroleum, b.p. 40–60° C.	Ether.		
Monoethylenic (oleic)	Soluble	Soluble	Dibromo-	28–30°
Diethylenic (linoleic)	Sparingly soluble	Soluble	Tetrabromo-	114° and liquid
Triethylenic (linolenic)	Insoluble	Almost insoluble	Hexabromo-	180–183° and liquid
Polyethylenic (4, 5, or 6)	Insoluble	Insoluble	Octa-, etc. bromo-	Darken at or above 200°

These properties have been made use of for qualitative determinations of the presence of oils containing glycerides of a characteristic degree of unsaturation. Thus, Hehner and Mitchell have given directions for the bromination of fatty oils under conditions somewhat of the following nature, the process being conveniently carried out in a 15–20 c.c. narrow stoppered graduated cylinder :

The oil (1 c.c.) is dissolved in 9 c.c. of ether and a 10

per cent. solution of bromine in glacial acetic acid is added until the colour of the bromine persists faintly, but permanently. A definite precipitate indicates the presence of oils containing linolenic or still more unsaturated acids, and the amount of the precipitate is a rough guide to the proportion of these constituents. Absence of any turbidity shows the absence of any but "non-drying oils," whilst a faint or definite turbidity usually indicates the presence in quantity of a "semi-drying oil" of the sunflower seed or cottonseed type.

If the method is applied to the mixed fatty acids from the oils the products are more definite in character and the test somewhat more precise; so much so that it has been suggested to make it quantitative by first separating the ether-insoluble bromides and then crystallizing the residue from the ethereal mother-liquors from petroleum ether. Increase in our knowledge of the properties of the bromo-additive compounds formed from linoleic and linolenic acids has shown that at best only about 50 per cent. of these acids are obtained in the respective forms of hexabromostearic acid insoluble in ether, or tetrabromostearic acid insoluble in petroleum ether; and that the actual yields obtained vary very much with the relative proportions of oleic and linoleic acid, oleic and linolenic acid, or linoleic and linolenic acid which may be present in the ternary mixture. The amount of ether-insoluble hexabromostearic acid or petrol-insoluble tetrabromostearic acid obtained in any given case is therefore a very indefinite criterion of the proportions of linolenic and linoleic acid in the original mixture, and the use of bromo-addition products of these fatty acids as an aid to their quantitative determination should now be abandoned. As an aid in the qualitative detection of ordinary linoleic and linolenic acids, however, they retain considerable value.

Determination of conjugated unsaturation.—The amount of conjugated unsaturated glycerides present in such fats as tung oil or oiticica oil can be determined by taking advantage of the fact that maleic anhydride unites with conjugated

systems to produce benzenoid compounds (Diels-Alder synthesis). Quantitative methods for determining the "diene" (Kaufmann) or "maleic anhydride" (Ellis and Jones) values of fatty oils have been given. Ellis and Jones reflux the oil with a 6 per cent. solution of maleic anhydride in toluene for 3 hours, whilst Kaufmann heats it with an acetone solution (1 per cent.) of the anhydride for 20 hours in a sealed tube at 100°. Details of the methods are given in the original papers, but it should be noted that maleic anhydride also exerts an acylating power, and that in presence of compounds containing free hydroxyl groups or of oxidized oils the maleic anhydride value observed is not necessarily wholly a measure of conjugated unsaturation.

Spectroscopic evidence is also useful in detecting conjugated aliphatic unsaturation in fatty oils. A system of three conjugated ethenoid bonds shows a marked absorption band at about $270m\mu$, whilst two adjacent ethylenic linkages lead to the production of an absorption band at about $230m\mu$.

3. Proportion of Water-soluble or Water-insoluble Volatile Fatty Acids present.—The methods involved under this head yield most important data for the edible fat analyst, enabling him to distinguish between butter fats, nut-oil fats of the coconut or palm kernel type, and other fats such as the common vegetable oils, tallow or lard. Consequently the details of these processes have been the subject of much careful work, and the comprehensive manuals previously referred to should be consulted before carrying out determinations of this kind. The chief methods which have proved of permanent value are merely summarized here, except that details are given of the standard Reichert-Meissl and Polenske processes.

In the first place, if the mixed fatty acids from a fat are washed repeatedly with hot water the acids of lower molecular weight (up to caprylic or capric acid) will be removed in solution, and the residual *water-insoluble fatty acids*, expressed as a percentage of the total fatty acids, were used by Hehner as a means of assessing the proportion of butter fat present in a mixture (*Hehner value*). The method

has not been so valuable, however, since the tropical nut-oil fats, which also contain fair amounts of water-soluble fatty acids, came into technical prominence.

The more modern methods depend on the proportion of the fatty acids which are volatile in steam (the acids up to and including lauric acid distil in a current of steam at atmospheric pressure, the latter, however, only to a small extent; of these butyric and caproic acids are soluble, and caprylic, capric (and lauric) acids insoluble in water).

The standard methods of determining the respective proportions of water-soluble and water-insoluble volatile fatty acids are due mainly to Reichert, Meissl, and Wollny on the one hand, and to Polenske on the other.

The Reichert-Meissl value is the number of c.c. of N/10 alkali required to neutralize the water-soluble volatile fatty acids obtained from 5 grms. of fat as follows:

The material (exactly 5 g.) is saponified completely in a 300 c.c. flask by means of 2 c.c. of 50 per cent. caustic soda solution in presence of 10 c.c. of 92 per cent. alcohol for 15 minutes, the alcohol then being evaporated and the dry soap dissolved in 100 c.c. of freshly-boiled water and acidified with 40 c.c. of normal sulphuric acid. The aqueous acid mixture is then distilled so that 110 c.c. of condensate are collected in as nearly as possible half an hour; the apparatus employed should be of the exact sizes and shapes indicated in the original papers of Wollny (or Polenske). The 110 c.c. of condensate is filtered (*cf.* Polenske value, below), and 100 c.c. of the filtrate is titrated against N/10 caustic alkali, with phenolphthalein as indicator.

The Reichert-Meissl value = $1 \cdot 1 \times$ number of c.c. N/10 alkali required.

The values obtained may vary from about 30 for butter fats to 5-8 for palm kernel and coconut oils, and about 0.5-1.0 for most other fats.

The methods used to distinguish between butter fats and tropical nut fats depend on the characteristic contents of butyric, caprylic, caproic, capric, and lauric acids in these materials.

Kirschner proposed to take advantage of the varying proportions of butyric and caproic (water-soluble volatile) acids from butter and from coconut oil, together with the insolubility of silver caprylate in water. The neutralized (titrated) 100 c.c. of filtered steam-distillate from the Reichert-Meissl determination is thoroughly shaken with 0.5 grm. of silver sulphate, set aside for one hour and filtered, when silver butyrate remains in solution. The filtrate and washings are acidified and steam-distilled according to an exact prescription and 100 c.c. of the distillate titrated as before with N/10 alkali. The figure so obtained is a measure of the *butyric acid* content of the fat.

Polenske's method allows both water-soluble and water-insoluble volatile acids to be estimated in one operation, and is conducted as follows :

The filtered fat (5 g.) is dissolved in 20 grms. of glycerine, 50 per cent. caustic soda solution (2 c.c.) is added, and the whole heated in a 300 c.c. flask over a Bunsen flame until saponification is complete. After cooling, warm recently-boiled water (90 c.c.) is added and all soap brought into solution (which should be nearly colourless), when 50 c.c. of 2½ per cent. dilute sulphuric acid and a little powdered pumice are added and the aqueous acid mixture is distilled in an apparatus of the dimensions stipulated by Polenske, so that 110 c.c. of condensate are collected in 20 (± 1) minutes. This condensate is cooled in water at 15° C. for about 15 minutes, mixed by gentle agitation, and filtered through a folded filter-paper (diameter 8 cm.) ; 100 c.c. of the filtrate is titrated with N/10 alkali, thus giving a measure of the water-soluble acids.

The acids which, although volatile in steam, are insoluble in water will be found (i) on the filter-paper, (ii) in the 110 c.c. condensate-flask, and (iii) on the inner surface of the condenser tube.

Three successive quantities of 15 c.c. of water are therefore washed through the condenser tube, into a graduated cylinder, thence into the 110 c.c. flask and over the filter-paper, the washings being rejected.

Next, three washings (15 c.c. each time) are similarly given with neutral 90 per cent. alcohol, the final filtrates through the 8 cm. paper being united and titrated against N/10 alkali.

The figure obtained, calculated to the number of c.c. ✓ of N/10 alkali required to neutralize the water-insoluble volatile fatty acids produced by the foregoing procedure from 5 grms. of fat, is known as the *Polenske value*.

It should be observed that the Reichert-Meissl and Polenske values are of an empirical nature and do not purport to indicate the whole of the amount of either water-soluble or water-insoluble fatty acids volatile in steam which are present in the original fat or wax. It is obvious that the separation by means of steam-distillation must at best be relative, since, if the distillation be continued until the last traces of one acid (*e.g.* caprylic) have come over, a certain amount of the next higher acid or acids will also have accompanied it; and, although the volatility in steam rapidly diminishes as the molecular weight increases, it is definitely appreciable up to lauric and myristic acids. Nevertheless, *by working under the controlled conditions as to dimensions of apparatus and time of distillation which have been laid down by the investigators of the methods* (*cf.* Bibliography), comparable results can be obtained which are an accurate index of the character of the fatty acids present in the original materials.

In both the Reichert-Meissl and Polenske determinations it is essential to carry out a blank estimation exactly as in the actual analysis, except that the fat or wax is omitted; the N/10 alkali thus required should not exceed 0.3 c.c.

The usual range of Reichert-Meissl and Polenske values for butter fats, nut fats, and ordinary vegetable oils is as follows:

			Water-soluble volatile acids, Reichert-Meissl value.	Water-insoluble volatile acids, Polenske value.
Butter fats 24-32	2-3
Coconut oil 7-8	15-17
Palm kernel oil 5-7	10-12
Oils such as olive or cottonseed 0.5-1.0	0.5

The Society of Public Analysts published in 1936 approved and revised details for the standard Polenske apparatus and for the exact procedure to be followed in determining Reichert-Meissl, Polenske and Kirschner values.

Other methods of assessing the low molecular weight acids characteristic of butter, coconut, palm kernel and similar fats have later been developed, but have not yet widely replaced the Reichert, Polenske and Kirschner values. These include the "A" and "B" values proposed by Bertram and the "butyric acid value" of Grossfeld.

In Bertram's method the mixed fatty acids are first converted into magnesium salts and the actual analysis carried out on the magnesium salts which are soluble in water. The amount of N/10 silver nitrate consumed in forming insoluble silver salts from an aliquot portion of the fatty acids from the soluble magnesium salts is the basis of the "A" value—indicative of the "nut oil" C₈ and C₁₀ acids. The amount of steam-volatile acids obtained, after another aliquot portion of the acids from the soluble magnesium salts has been shaken with silver sulphate, filtered, and the aqueous filtrate acidified with sulphuric acid and steam-distilled, is the basis of the "B" value—which, according to Bertram, indicates about 98 per cent. of the actual butyric acid present.

Grossfeld salts out the soap solutions from the saponified fat with excess of sodium sulphate, and uses an aliquot part of the aqueous saline layer only for acidification and subsequent steam-distillation. The acidity of the distillate or "butyric acid value" is said to be a close estimate of the butyric acid present and the analysis can be carried out on 1.5 g. or less of fat.

For further details of these procedures the original literature must be consulted.

4. Acetyl Value.—The acetyl value is the number of milligrams of potassium hydroxide required to neutralize the acetic acid produced by hydrolysis of one gram of an acetylated fat or wax.

It is thus an indication of alcoholic hydroxylic groups

(although care must be taken, in cases where free fatty acids are present, that carboxylic hydroxyl is not included in the estimation owing to the production (and incomplete hydrolysis with water) of mixed acetic-fatty acid anhydrides during acetylation). The following types of compounds will therefore be registered by the acetyl value determination : hydroxylic fatty acids or glycerides and esters, free alcohols (either higher fatty alcohols or sterols), mono- and di-glycerides, oxidized or rancid fats.

As already mentioned, the acetyl value is a *characteristic* of a few fats (notably castor oil and croton oil), but for the majority it is a *variable* and indicates the presence of adventitious alcoholic bodies rather than essential constituents of the natural fats or waxes.

The determination is carried out as follows :

The sample (about 10 g.) is boiled with 20 grms. of acetic anhydride for two hours under a reflux condenser ; the cooled product is poured into 500-600 c.c. of hot water in a large beaker and boiled gently for half an hour in presence of a little porous pot. The aqueous layer is settled and drawn off and the washing process repeated similarly three or four times, or until the aqueous layer is finally neutral to litmus-paper. The acetylated oily layer is then filtered through a dry paper and dried in a steam-oven for a short time.

The dried acetylated product (about 5 g.) is then saponified exactly as in the determination of the saponification equivalent of a fat (p. 42), but when hydrolysis is complete the alcohol is distilled off and the soap taken up in water. The acetic acid, which is now present as potassium acetate and whose quantity is to be determined, may be isolated in either of the two following ways, the first being more rapid and equally accurate if carefully carried out :

(i) *Solution Process.*—Add to the soap solution a volume of normal sulphuric acid exactly 1 c.c. in excess of that equivalent to the alcoholic alkali originally added (if this be done as a titration prior to removal of the alcohol the saponification equivalent of the acetylated product, which

is sometimes a useful figure in the case of wax alcohols or pure hydroxylated glycerides, may be obtained at the same time). On warming the acidified *aqueous* solution gently, the fatty acids will separate as an oily layer ; the aqueous acid layer is drawn off in a separating funnel and the fatty acids washed with hot water until the aqueous washings are neutral to litmus. The united aqueous layers (including the first) are titrated with N/10 alkali. After deducting the requisite correction for the known excess of standard mineral acid used in acidifying, the acetyl value is readily calculated :

Acetyl value

$$\frac{\text{c.c. of N/10 KOH used to neutralize acetic acid} \times 5.6}{\text{wt. of acetylated product taken}}$$

(ii) *Distillation Process.*—The aqueous soap solution is rendered freely acid with dilute sulphuric acid and steam-distilled until 100 c.c. of distillate require no more than 0.1 c.c. of N/10 KOH for neutralization. Usually 600-800 c.c. of condensate will be required. The united aqueous distillates are titrated to phenolphthalein with N/10 alkali

$$\text{and the acetyl value} = \frac{\text{c.c. of N/10 KOH} \times 5.6}{\text{wt. of acetylated product taken}}$$

The following precautions should be observed in determining the acetyl value of a fat or wax :

(i) In consequence of the large proportion of water used in either process of separation of the liberated acetic acid, it is necessary to ensure that the water does not contain any dissolved carbon dioxide by vigorous boiling before use, either for washing the fatty acids or for generating steam for the distillation. Otherwise there will be introduced a definite error in the final titration with N/10 alkali.

(ii) If the original fat contains volatile water-soluble fatty acids (butter or nut fats), these will also appear with the acetic acid in the final aqueous solution. In such cases a blank determination must be made on the original fat (*i.e.* without acetylation) and the value obtained deducted

from that obtained in the acetyl value titration on a basis of equal weights of original material.

Franchimont preferred to acetylate the fat in acetic anhydride in the presence of a few drops of concentrated sulphuric acid, whilst Verley and Bölsing have recommended acetylation of the fat with acetic anhydride dissolved in pyridine; Kaufmann and Funke add, for the acetylation, a double excess of acetyl chloride in toluene to the fat dissolved in pyridine and heat at 65–70° for 15 minutes. The pyridine-acetic anhydride method appears to have advantages over the older method in the ease with which the acetylated fat can be isolated free from acetic acid or anhydride.

5. Content of "Unsaponifiable" Matter.—This may be determined in conjunction with the saponification equivalent estimation or, if the amount of "unsaponifiable" matter is below 1 per cent., it is better carried out on a separate sample of about 10 grms. of material which is saponified by alcoholic potash as in the saponification equivalent test (p. 42).

In either case the alcohol is distilled off and the residue taken up in about 200 c.c. of water and placed in a 500 c.c. separator; ether (200 c.c.) is added, and the whole shaken gently with a horizontal swirling motion. If undue emulsion forms, a few drops of alcohol and/or brine should be added.

When the ethereal and aqueous layers have separated sharply, separation is effected and the aqueous layer re-extracted twice in the same manner with the same volume of fresh ether. The ether extracts are united, washed once with water to remove traces of soap and then concentrated and finally heated in the steam-oven in a tared flask until the weight is constant.

Alternatively, the residual saponified product (after removal of as much alcohol as possible) is mixed with half its weight of pure sand and dried in a basin until friable and then extracted with ether in a Soxhlet cup.

The extract is washed with water to remove traces of soap and dealt with as above.

A committee of the Society of Public Analysts reviewed in 1933 the methods suitable for the determination of unsaponifiable matter and published in full detail a standard method applicable to as many types of fat as possible, supplemented by minor modifications for use in certain special instances.

It must be pointed out that the description of "unsaponifiable" matter is a misnomer, since the above methods really determine the amount of neutral (non-acidic) material, insoluble in water, present, either free or combined with fatty acid, in the original material.

In cases where large amounts of higher fatty alcohols or sterols are present as esters (*e.g.* sperm oil, beeswax, carnauba and many other waxes, or wool grease), the combined alcohols in question are registered as "unsaponifiable" matter in the above estimation.

In addition, of course, this process gives a measure of any free sterols or other water-insoluble alcohols, hydrocarbons, or other neutral organic compounds present in the materials examined.

6. Analysis of Glycerol.—The analytical control of glycerol is another case of specialized methods which have been devised to afford rigorous control of its suitability either in the manufacture of nitroglycerine or for use in pharmacy and medicine. Tests of this kind, which are mainly directed to the exclusion of harmful impurities from either point of view (*e.g.* trimethylene glycol, moisture, etc., in dynamite glycerine, or arsenic, lead, etc., in pharmaceutical glycerine) are referred to in the section dealing with glycerine technology.

The methods which will be discussed here are those which are directed to give the measure of actual glycerol present in a given case. They are all more or less based on the *a priori* assumption that glycerol is in fact the substance which is being determined, and therefore it is necessary to be certain that this assumption is justified, because materials likely to accompany glycerol in practice would equally well react similarly under the conditions of the tests.

The methods of determination which have been put forward are mainly as follows :

1. Oxidation with potassium dichromate and sulphuric acid (Hehner).
2. The acetin process (Benedikt-Cantor).
3. The isopropyl iodide process (Zeisel-Fanto).
4. Isolation as glycerol (Shukow and Schestakow).

The first method gives excellent results, but will also serve to oxidize many other organic compounds (trimethylene glycol, celluloses, sugars, and other hydroxylated bodies) to carbon dioxide and water in the same manner.

The second method also gives trustworthy data, but registers at the same time other hydroxylic compounds of a similar chemical nature to glycerol.

Since, however, it is usually possible to obtain the glycerol in such a form that it can be known that only trimethylene glycol (or propylene glycol) will be simultaneously present, the application of both the dichromate and the acetin process serves to afford the data from which the proportion of glycerol and of trimethylene glycol can be calculated. These methods have received the recommendation of an International Committee on Glycerine Analysis which met in 1911 to standardize this subject as far as possible.

The isopropyl iodide process, which depends on the quantitative conversion of glycerol into isopropyl iodide and the decomposition of the latter by alcoholic silver nitrate in a closely similar manner to Zeisel's method of determination of methoxyl and ethoxyl groups, is more tedious than the other methods and probably less accurate ; whilst it is still open to the original objection that the assumption is involved that only glycerol is responsible for the changes which occur, since glycerol is estimated in terms of the silver iodide produced.

Finally, the Shukow-Shestakow process simply consists in evaporation of the neutralized aqueous lye from the saponification of a fat or wax until it contains 40-50 per cent. of glycerol, mixing this concentrate with its own

weight of freshly ignited, powdered anhydrous sodium sulphate, powdering the mixture and extracting with pure acetone in a specially constructed Soxhlet extractor made entirely of glass. The acetone solution, after about five hours' extraction, is concentrated and dried to constant weight in a steam-oven. This method is liable to give somewhat high results, owing to the opportunities for absorption of other organic compounds by the acetone, for formation of small quantities of high-boiling condensation products of acetone, or for absorption of water vapour. It is, however, useful as a rough guide to the glycerol content of fatty materials.

More precise details must be given of the determination of glycerol by the standard dichromate and acetic processes:

The fatty material to be investigated (about 20 g.) is saponified with alcoholic potash as in the determination of the saponification equivalent, the alcohol is removed, and the aqueous soap solution decomposed with dilute sulphuric acid. The fatty acids are washed and the aqueous acid liquor and washings united, placed in a basin, neutralized with excess of barium or calcium carbonates, and evaporated down on the water-bath until pasty, when it is extracted thoroughly with a mixture of ether and alcohol. The mixed solvent is removed from the filtered extract by distillation on a steam-bath and the residue left in a desiccator and then weighed.

This procedure suffices in the ordinary case where the original material is a pure fat or soap-lye emanating solely from fatty materials. If, however, the glycerol is suspected to be contaminated with substances of carbohydrate origin it should be distilled, preferably in a current of superheated steam, under as low a pressure as is possible, and the whole of the glycerol collected in the distillate, which, so long as its weight is known, need not be of any definite concentration, providing that the glycerol content is at least 70-75 per cent.

(i) *Analysis of the Crude or Distilled Glycerine by the Dichromate Method.*—Crude glycerine (20 g.) is weighed

and made up to 250 c.c. with water. This solution (25 c.c.) is mixed with silver carbonate (prepared for each test from 140 c.c. of 0·5 per cent. silver sulphate solution precipitated by 4·9 c.c. normal sodium carbonate, settled, decanted, and washed by decantation), shaken and set aside for a few minutes, after which a 10 per cent. solution of basic lead acetate (about 5 c.c.) is added and the mixture again left for about 10 minutes. It is then made up to 100·15 c.c. with distilled water, well shaken and filtered into a flask (the filtrate should not give any turbidity on addition of more lead acetate, otherwise it is necessary to repeat the process on a fresh 25 c.c. sample, using more of the latter precipitant).

25 c.c. of the filtrate is placed in a clean flask and acidified with 12 drops of 20 per cent. sulphuric acid, after which pure potassium dichromate (3·7282 g.) is added, rinsing down with 25 c.c. of water; 50 c.c. of 50 per cent. sulphuric acid (by volume) is added and the flask immersed in boiling water for 2 hours. A slight excess of standard ferrous ammonium sulphate solution is added (ensuring excess by employing a dilute potassium ferricyanide solution as external indicator) and the excess is titrated back with standard dichromate (7·4564 g. $K_2Cr_2O_7$ per litre).

1 g. dichromate = 0·13411 g. glycerol or 1 g. glycerol = 7·4564 g. dichromate.

(ii) *Analysis of the Crude or Distilled Glycerine by the Acetin Method.*—Commercial crude glycerine, or the glycerine prepared as above (about 1·5 g.), is accurately weighed into a 100 c.c. round-bottomed flask and boiled for 1½ hours under a reflux condenser with about 10 c.c. of acetic anhydride and 3 g. of anhydrous sodium acetate. As in determining acetyl values, the excess of acetic anhydride has now to be decomposed with water, but in the present case triacetin is much more susceptible to hydrolysis than the alcoholic acetyl derivatives of the higher fatty acids, and is also slightly volatile in steam. The reaction mixture is therefore cooled and some recently boiled water is added, and the warm mixture is filtered into

a 500 c.c. flask and washed with freshly boiled water, after which it is allowed to cool and neutralized as rapidly and accurately as possible with a dilute (2 per cent.) solution of caustic soda, taking care to avoid any local excess of alkali by vigorous agitation during the addition of the latter. Phenolphthalein is used as indicator and the neutral point must not be overpassed, or an erroneous result will accrue.

Normal caustic soda solution (50 c.c.) is added and the solution boiled for 15 minutes and titrated with normal sulphuric acid. A further 50 c.c. of the normal alkali is similarly boiled and titrated against normal acid, the difference in the two readings indicating the amount of alkali used in hydrolysis of the triacetin present.

1 c.c. of normal acid corresponds to 0.03069 g. glycerol (and to 0.03800 g. trimethylene glycol).

The percentage of glycerol in the crude sample examined can then be calculated, and a further calculation will give the percentage of glycerol produced from the original fatty material.

If the glycerol figures from the dichromate and acetin analyses do not agree within the limits of experimental error, the presence of trimethylene glycol will be suspected. The amount of glycerol and of trimethylene glycol can also be calculated by combining the results by both methods, two simultaneous equations involving two unknown quantities being available.

7. Analysis of Rosin.—The soap analyst frequently has to determine the proportion of rosin acids in the mixture of fatty acids present in a soap. For this purpose the method worked out by Twitchell is most useful, although the order of accuracy to be obtained is not so high as in most of the foregoing analyses.

Fatty acids are very readily esterified by means of alcoholic hydrochloric acid, whereas the rosin acids are only esterified with great difficulty.

The dry mixed fatty and rosin acids (about 3 g.) are therefore accurately weighed and dissolved in 30 c.c. of absolute alcohol; a stream of dry hydrogen chloride is

passed through the solution, cooled in running tap-water, for about an hour and left to stand for a further hour. Water is now added and the mixture (about 150 c.c.) boiled in order to clarify it.

The mixture may then be transferred to a separator, the flask being washed out with about 150 c.c. of ether; the ethereal solution of the products of the reaction is washed with water until the wash-waters are neutral, when the bulk of the ether is evaporated, 50 c.c. of neutralized alcohol added, and the solution titrated to phenolphthalein with standard caustic alkali. The mean equivalent of the rosin acids is usually taken as 346, and

$$\text{the percentage of rosin acids} = \frac{\text{c.c N alkali} \times 0.346}{\text{wt. of mixed acids}}$$

Alternatively, the diluted aqueous-alcoholic mixture may be extracted with petroleum ether, the extract washed with water and extracted with a dilute solution of caustic potash containing a little alcohol. The rosin acids will thus be converted to rosin soap in dilute solution, from which the rosin acids may be recovered by acidification and extraction with ether, dried, and weighed as such. This method avoids any inaccuracy due to the assumed equivalent of the rosin acids, but is no more accurate otherwise than the titration process.

Wolff and Scholze dissolve the mixed fatty and rosin acids (2-5 g.) in methyl alcohol (10-20 c.c.) and boil for two minutes in presence of a solution (5-10 c.c.) of 20 per cent. methyl alcoholic sulphuric acid. The unesterified rosin acids are determined by titration with N/2 alcoholic potash. They are then submitted to a repetition of the esterification process to remove any unesterified fatty acids, and the rosin acids recovered and weighed. The mean of the two determinations gives a close approximation to the true proportion of rosin acids present.

McNicoll employs for the esterification of the fatty acids a 4 per cent. solution of naphthalene- β -sulphonic acid in absolute methyl alcohol (20 c.c.), heated with the mixed

fatty and rosin acids (2 g.) under reflux for 30 minutes. The product, and a "blank" solution similarly refluxed, are titrated with N/2 methyl alcoholic potash and the rosin acids calculated as in the Twitchell method; the rosin soaps are separated from the fatty acid esters by extraction of the latter with a mixture of ether and petrol, and subsequently reconverted to acids, isolated and weighed, as a check on the volumetric determination.

One or other of these modifications of the original Twitchell method is usually preferred nowadays.

SOME SPECIFIC CHEMICAL TESTS

Of the very large number of methods of this kind which have been proposed we shall only refer to the following :

Thermal Tests : Maumené, bromine, and Mackey tests.

Solubility Tests : Valenta and Crismer tests.

Colour Tests : Baudouin, Halphen, and Liebermann-Storch reactions.

Thermal Tests.—These depend on the fact that most of the additive actions of unsaturated glycerides or fatty acids are exothermal in character, and by carrying such actions out under controlled conditions the heat evolved (*i.e.* the rise in temperature) serves as a semi-quantitative guide to the nature of the materials present.

In the *Maumené test* the rise of temperature obtained on mixing fatty acids with concentrated sulphuric acid is the criterion of the amount of unsaturation present. In order to obtain concordant results, it is necessary to employ sulphuric acid of exactly known concentration and to bring both acid and fatty oil to the same temperature before mixing.

The apparatus recommended by Archbutt for the test is a glass beaker of about 200 c.c. capacity packed into a larger vessel, the intervening space being filled with cotton wool or loose asbestos. The oil under examination (50 g.) is placed in the beaker and 10 c.c. of the concentrated sulphuric acid added from a pipette whilst the oil and acid are vigorously stirred by a thermometer. The temperature rises to a maximum which is noted.

This test is falling into disuse, since it merely gives a qualitative guide to the degree of unsaturation, which can at present be ascertained almost as expeditiously with quantitative accuracy by rapid determination of the iodine absorption.

Some idea of the rise of temperature afforded by the test will be obtained from the following approximate values :

	Iod. Absn.	Rise in ° C.
Olive oil	83	42°
Rape oil	105	60°
Cottonseed oil	110	80°
Soya bean oil	130	90°
Linseed oil	180	110°
Whale oil	120	90°
Lard	60	30°

The bromine thermal test, due to Hehner and Mitchell, is distinctly more accurate in nature than the Maumené test and is very rapidly carried out, so that it finds a certain use in rapid preliminary examination of fatty oils prior to formal determination of their iodine absorption.

1 grm. of oil is dissolved in 10 c.c. of chloroform and placed in a small Dewar vacuum tube. 1 c.c. of bromine is carefully added by means of a special pipette and the mixture stirred with a thermometer graduated in tenths of a degree. The temperature rises very rapidly, and the rise in temperature bears a definite ratio to the iodine absorption of the oil. Employing the above quantities, it is found that rise in temperature ($^{\circ}$ C.) $\times 5.5$ = iodine absorption per cent.

The factor 5.5 is empirical and depends on the quantities of reagents used, and to some extent on the apparatus ; it is found, however, that by working on a material of known iodine absorption a factor may be obtained (as a rule approximating to 5.5-6.0) for the particular apparatus, which permits the test to be used as a rapid first approximation to the true iodine numbers of most oils.

The *Mackey test* (referred to in detail in Section IX., Chapter III., p. 506) is a practical means much used in ascertaining the suitability of fatty oils to be applied to textiles. Such oils, if their content of linoleic or other polyethylenic glycerides be above a certain proportion, may

develop sufficient heat, due to their atmospheric oxidation when in films on the textile fibre, to cause spontaneous ignition of the latter. The test, in its original form, consists in maintaining a standard mass (7 g.) of cotton wool, impregnated with the oil (14 g.) and subjected to controlled air-flow in a standard apparatus, at 100° for one hour, during which time it should not develop a temperature more than a few degrees above 100°. Later forms of the method include the plotting of a temperature-time curve covering the development of temperatures between 100° and 200°, the rate of increase of the temperature due to oxidation of the exposed film being equally or more informative than the final temperature attained.

Solubility Tests.—The temperature at which a fatty oil becomes completely soluble in certain organic solvents, or "*critical solution temperature*," affords some indication of the character of the oils. In the Valenta test the solvent is glacial acetic acid, whilst Crismer has worked out similar data for the critical solution temperatures of fatty oils in alcohol. The large manuals of fat analysis should be consulted for details of these methods.

Colour Tests.—In the bygone days when fat analysis was less systematic than it is at present, and when the total number of fats and waxes in general technical use was much smaller than at present, much reliance was reasonably placed on certain specific colour reactions displayed by definite classes of fats or waxes. With the increase in the varieties of natural materials at the command of the industry the validity of such tests, except in rare instances, has diminished to a great extent, although fresh "*characteristic reactions*" appear in the literature in bewildering abundance. This kind of test has, however, reached the limit of its usefulness in most cases, owing to its lack of precision and its capacity for yielding positive results with materials other than those for which it is supposed to be characteristic, and the extended use of colour reactions is to be deprecated in favour of the development of more fundamental and scientific methods of analysis.

Three only of the more especially useful and definite methods of the kind will therefore be indicated here: and these more by way of illustration of principle than as recommendation for their use.

Baudouin Colour Test for Sesame Oil.—This is one of the most definite colour reactions, so much so that some Continental countries insist on the presence of 10 per cent. of this oil in artificial butter fats in order to facilitate the analytical detection of the latter; nevertheless a few other oils and certain other materials are capable of responding positively to the test.

A small portion of the fat is boiled with concentrated hydrochloric acid and a few drops of an alcoholic solution of furfural are added; the appearance of a red colour indicates the presence of sesame oil.

Halphen Colour Test for Cottonseed and Kapok Oils.—This reaction is fairly characteristic for oils from the *Gossypium* and allied families, but may also be given faintly by true butter fats or lards from animals which have been fed largely on cottonseed cake.

A small sample of the fat is boiled with an equal bulk of butyl (or a mixture of ethyl and amyl) alcohol, and an equal volume of carbon disulphide containing about 2 per cent. of free sulphur is then added to the hot solution; excess of carbon disulphide solution is evaporated on a water-bath, and the mixture then heated for 20 minutes in boiling brine. A reddish or orange-red coloration indicates cottonseed or kapok oil.

Liebermann-Storch Test.—1-2 c.c. of the sample are gently warmed in a test-tube with acetic anhydride and cooled; the acetic anhydride layer is withdrawn to another tube, in which it is mixed with a drop of 62 per cent. sulphuric acid. Production of a violet-green colour indicates cholesterol, sitosterol, or rosin acids; a green colour may indicate isoocholesterol. Violet-green or pink colorations are also given with many other terpene derivatives, and this reaction, which is one of the most famous of the older colour tests, is an excellent example of their limitations.

PHYSICAL TESTS

i. Setting point and Melting point of Fats and Waxes and of the Corresponding Fatty Acid Mixtures contained therein.—Since the great majority of natural fats or their corresponding fatty acids are more or less complex mixtures, there is little possibility of obtaining a sharp melting point of the character exhibited by highly crystalline individual carbon compounds, and the methods of determination of this property are therefore somewhat specialized. It is also found that the setting points of the fats or fatty acids are definitely more characteristic than the melting points, and although determination of the setting point is a more lengthy operation than that of melting point, it should be preferred where possible. Indeed, the setting point of the mixture of fatty acids contained in a fat, or "titer" as it is technically termed, is widely used in commerce as the basis of valuation of many fats, especially tallow.

In order to obtain concordant results in the setting point determination it is necessary to carry out the operation in a standardized manner, and the following method, due to Dalican and F. Tate, is in general use in English laboratories :

The fat (50 g.) is saponified in an open basin by boiling with a mixture of 45 c.c. of 30 per cent. caustic soda solution and 45 c.c. of alcohol, and the contents are finally evaporated with stirring until the residual soap is dry. It is then converted into fatty acids in the usual way, and the latter are separated from aqueous acid and washed free from mineral acid with hot water. The washed fatty acids are filtered through a dry filter-paper and dried at 100°C . for 2 hours, and then transferred to a titer glass.

The titer glass is 9 cm. deep and 2.75 cm. diameter, with sides 0.30 cm. thick, and is provided with a flange about 5 cm. wide round the top. The glass rests by means of the flange on an asbestos, wooden, or ebonite cover which fits over an outer glass beaker 13 cm. deep and 10 cm. wide,

thus leaving an annular air-insulation space between the two vessels.

The fatty acids in the titer glass are allowed to cool with steady stirring by means of the thermometer employed (which should be calibrated in fifths or tenths of a degree C.) until the temperature ceases to fall or until the acids become so turbid that the thermometer stem can barely be seen when in the centre of the titer glass. The thermometer is then clamped so that the bulb is exactly in the centre of the fatty acids and its reading noted carefully ; as the acids solidify, the temperature commences to rise and eventually reaches a maximum steady figure which is the *tier* or *solidifying point of the fatty acids*.

The same apparatus may be used to observe the setting points of the natural fats and waxes themselves, but in the case of the latter the rise in temperature, although usually quite perceptible, is not so well marked as in the case of the fatty acids.

As already stated, there is no sharp melting point in the case of most fats or their composite fatty acids, but comparable, approximate melting points may be ascertained by either of the following methods :

(a) *Closed Capillary Tube*.—In the cases of very hard fats, waxes, and fatty acids the substance may be inserted in the closed end of a capillary tube in the ordinary way, and the temperature at which the liquefied material becomes definitely clear is taken as the "melting point."

(b) *Open Capillary Tube*.—A pair of capillary tubes, open at both ends, are dipped into the melted material until a column of fat 1 cm. in length is present. The tubes, which should be of as nearly as possible the same internal diameter in all cases, are set aside at room temperature for 10-12 hours, or at 0° for 3-4 hours, and are then fastened to a thermometer so that the lower ends are on a level with the end of the bulb. The thermometer is then clamped so that the lower end of the tubes and bulb are 3 cm. below the surface of water in a beaker. The water is heated slowly at the rate of about 0.5° C. per minute, and the

temperature at which the contents of the tubes become sufficiently mobile to rise under the hydrostatic pressure of the water is recorded as the "melting point."

It is advisable to carry out this process on two tubes in order to eliminate the possibility of a badly filled semi-adherent column of fat slipping up the tube at too low a temperature.

(c) *Thermometer Bulb Method*.—The solid material is scraped delicately with a fine knife point and the scrapings transferred so as to cover about half of the bulb of a thermometer. The latter is then clamped inside an empty test-tube which is immersed in a beaker of water, and the latter is carefully heated so that the temperature rises about 0.5° C. per minute. The "melting point" is the temperature at which the fat particles coalesce and run down to produce a clear drop at the lowest point of the thermometer bulb.

Either of these methods, especially (b) and (c), give quite concordant results amongst themselves in practised hands, but the actual values obtained by each method for the same material are not necessarily the same. It is to be emphasized that the fatty material must always have been in the solid state for 10–12 hours at room temperature, or for 3–4 hours at 0° C., prior to determination of the melting point being carried out.

2. Specific Gravity of Fats and Waxes.—The specific gravity of fats and waxes does not vary as a general rule to an extent which makes this property useful in discriminating between one fat and another, but it is not infrequently required for various purposes.

It is best determined, when sufficient material is available, in a specific gravity bottle of 25 or 50 c.c. capacity; a figure of high accuracy is thus readily obtained, and the time taken is little longer than that required for some of the other methods.

If only a small amount of sample is available, a Sprengel tube pycnometer may be substituted for the specific gravity bottle, with little or no loss of accuracy.

Somewhat more rapid results may be obtained by the

use of the Westphal balance, using a metal plummet which displaces a known volume of liquid, or by the employment of a hydrometer floated in the liquid material. The hydrometer method is not to be recommended for fatty oils, however, except as a very rough guide.

If only very small amounts of material are available, one drop may be suspended in alcohol and water added drop by drop until the oil just commences to rise: the specific gravity of the alcohol-water mixture is then determined by gravity bottle or Westphal balance, and indicates that of the oil droplet.

The temperatures at which densities have been recorded vary somewhat widely; liquid fats have usually been determined at 15° C., sometimes at 20° or 25° C. It is probably useless to reiterate a plea that the physico-chemical standard temperature of 25° C. should be generally adopted in technical practice: in fat analysis, in addition to the universal bugbear of maintaining a temperature of 15° C. in hot summer days, the use of 25° C. would permit of many semi-liquid materials being measured readily in the liquid state.

Solid fats and waxes have been measured mainly at 40°, 60°, and 100° C.

In filling a pycnometer or gravity bottle with liquid fat, it is essential to ensure removal of all minute air-bubbles by leaving the vessel in the thermostat for a few minutes to allow them slowly to reach the top and finally to displace with more fat if necessary.

Solid fats, of course, are filled into the apparatus in the melted state, and it is well to carry out the measurement at not less than 5-10° C. above their melting point. The measuring vessel should be calibrated with water at the temperature of measurement, and it is then easy to calculate from the tables the density of the material at this temperature with respect to water at any of the more conventional temperatures.

The specific gravity of practically all the fats and waxes lies between 0.90 and 0.95.

3. Refractive Index of Fats and Waxes.—The refractive power of fats and waxes varies somewhat widely and is chiefly governed by the proportion and degree of unsaturated matter present. It is thus characteristic for various classes of fats and is much used in butter analysis ; it also provides the most rapid means of following the progress of hydrogenation of a fat except actual continuous measurement of the hydrogen absorbed (which is not practicable as a rule on the large scale). Consequently the measurement of refractive index is a matter which should be familiar to the fat-chemist.

The actual measurement is simple, as the instruments are supplied with scales which read directly and to several places of decimals either the index of refraction, or an arbitrary scale of "degrees," and it is only necessary to conform with the directions supplied by the makers.

Of the refractometers in general use may be mentioned :

(a) The *Pulfrich* refractometer, in which the angle of refraction between the liquid and a highly refracting prism face is directly measured ; this instrument is not used to any extent in technical analysis.

(b) The *Abbé* refractometer, in which the index of refraction is read off directly from observation of the total reflection which a thin film of liquid placed between two prisms of a glass of high refractivity produces in transmitted light.

(c) The *Zeiss* butyrorefractometer, which is essentially a type of Abbé instrument designed to cover a more limited range than the latter (namely, that of butter and butter substitutes), with consequent greater accuracy in the individual graduations. The scale is graduated in arbitrary "butyrorefractometer degrees," which can be converted if desired to refractive indices.

(d) The *Amagat-Jeans* oleorefractometer, a more cumbersome type of instrument which has now passed out of general use, although many of the older refractivities are still in the literature in the form of "oleorefractometer degrees."

The Abbé and Zeiss instruments are practically universally employed at the present time, and consist essentially of two highly polished prisms hinged together and surrounded by a jacket through which water at constant temperature can be passed. A determination is made by opening the hinged prisms, very cautiously but thoroughly cleaning the prism faces with a little ether applied on a soft silk cloth or soft chamois leather, and placing two or three drops of the filtered liquid fat on the horizontal face. The prism is then closed and the apparatus left for two or three minutes to ensure that the oil has reached the temperature of the jacket, and the reading is then directly made by rotating the focusing telescope until the line of total reflection passes through the intersection of two hair-lines fixed in the field of view.

As with specific gravities, refractivities have been given at various temperatures, but for fats it is becoming general to adopt 40° C. as the standard temperature. This is a particularly suitable temperature because it serves for all except the hardest fats and waxes, whilst the members of the important and numerous class of soft fats, including butters and butter substitutes, are completely liquid and transparent at this temperature.

The following table will serve to correlate refractive indices with butyrorefractometer and oleorefractometer degrees :

Refr. index.	Butyrorefractometer.	Oleorefractometer.
1·422	0·0	—
1·425	3·7	—
1·430	10·0	—
1·435	16·4	—
1·440	23·0	—
1·445	29·7	—
1·450	36·7	—
1·455	43·7	—
1·460	51·0	-53
1·465	58·6	-20
1·470	66·4	-3·5
1·475	74·3	17
1·480	82·9	39
1·485	91·8	61
1·490	(over 100)	61

It may be mentioned here that in recent years it has been proposed to utilize refractive index as a rapid method in determining the oil content of seeds (Leithe, Groenhof, Scharrer, etc.). A weighed quantity of the seed is ground with sand and an equal weight of a suitable organic solvent (bromonaphthalene, chloronaphthalene, tetralin, etc.). The refractive index of the filtered solution of the fatty oil in the solvent is measured, preferably in a Zeiss immersion refractometer reading to 0·00001, and the percentage of oil calculated from the known refractive indices of the oil in question and the solvent used.

4. Viscosity of Fats and Waxes.—This property is chiefly of technical value in connection with lubricants, but it is occasionally determined in other cases and an indication of the chief methods of measurement available will therefore be given.

There is a welcome tendency to refer viscosity to absolute units instead of relative comparison with water, or to the statement of the mere time of flow under stipulated conditions in a standard apparatus.

The absolute unit of viscosity in the C.G.S. system is termed the *poise*, and for technical purposes Bingham and Jackson have suggested that a unit one-hundredth of this is more convenient, *i.e.* the *centipoise* (*cP*). Archbutt has pointed out that the absolute viscosity of water at 20° C. is 1·005 *cP*. and at 20·2° C. 1·000 *cP*., so that if viscosities are measured at 20·2° C. the relative viscosity compared with that of water and the absolute viscosity in centipoises are numerically identical. Where possible, therefore, it would seem convenient to determine viscosities at this temperature.

Capillary Viscosimeters.—The most accurate method is to determine the time of flow of a given volume of the liquid material under its own head through a capillary tube at a given temperature. The apparatus employed is usually that devised by Ostwald, and consists of a glass U-tube fitted with an upper bulb in one limb and a lower bulb in the other, a length of capillary tube being inserted

immediately beneath the upper bulb, which is graduated by two lines above and below it.

If n , t , and d are the absolute viscosity, time of flow, and specific gravity of the fat, etc., and n_1 , t_1 , and d_1 are the absolute viscosity, time of flow, and specific gravity of the water, then the absolute viscosity of the fat $n = \frac{td}{t_1 d_1} \times n_1$.

Disregarding n_1 , the expression gives the viscosity of the oil relative to that of water.

It is often objected that the time of flow in this apparatus is too slow for rapid analytical measurements, but by employing a capillary tube of suitable width and calibrating against a viscous fluid of known viscosity such as pure glycerol or similar substance, this difficulty can be avoided.

Falling Sphere Viscosimeter.—For very viscous fluids measurement of the time taken by a metal sphere of exactly known diameter to fall through a definite depth of liquid affords a very accurate means of determining viscosity, and an apparatus and method of use has been described for this purpose by Gibson. The majority of fatty oils are probably, however, too mobile to be adapted to this method.

Efflux Viscosimeters.—The viscosimeters almost wholly used in technical practice do not give a measure of absolute viscosity in C.G.S. units, but give arbitrary figures for the time taken for a definite volume of liquid to flow through an open orifice of standardized dimensions. For this purpose standard types of apparatus have been devised by various workers, which are supplied to their exact specifications by purveyors of laboratory apparatus: Redwood's viscosimeter is widely used in the British Empire, Engler's in Germany, Saybolt's in America, and Barbey's in France.

The principle of the methods of use is much the same in the case of the first three, and full details of manipulation may be obtained in the larger analytical treatises to which references are given in the Bibliography.

In the Redwood apparatus the oil is contained in a silvered-copper vessel immersed in a bath which can be maintained at any desired temperature (measurements are

usually made at 70°, 120°, or 180° F., and the instrument is constructed to deliver 50 c.c. of standard sperm oil at 70° F. in 100 seconds). In the centre of the base of the metal container is set an agate jet of standard diameter, which can be closed at will by a metal ball valve attached to a clamped vertical rod. The jet must be kept perfectly clean and treated with extreme care to avoid accidental scratching and alteration in diameter.

The metal vessel is filled with the clear filtered material under test exactly up to a point fixed inside the vessel, and the liquid must occupy exactly this volume when it has attained the temperature of the determination.

The ball valve is then raised and 50 c.c. of the liquid is allowed to flow into a graduated flask; the time of efflux of the 50 c.c. is measured by a stop-watch, two or three determinations being made to ensure an accurate mean reading.

CHAPTER V.—THE RESOLUTION OF FATS AND WAXES INTO THEIR COMPONENT ALCOHOLS AND ACIDS

Introductory.—The standard methods of fat analysis, of which some details have been given in the preceding chapter, are those upon which the industrialist relies for the assessment of the values of the raw materials and fat products with which he is concerned. It will be plain, however, that almost without exception these analytical characteristics, whilst exceedingly useful as criteria of various technical properties, afford no direct indication of the actual chemical structure of the materials in question.

It must be equally self-evident that the technical operator who is concerned to transform the natural materials into soaps, paints, or the numerous other outlets of the oils and fats industry, will require a more thorough and individual knowledge of his raw materials than is revealed by the ordinary methods of analysis.

It is therefore considered well to devote a few pages to some indication of the methods by which the fats and waxes may be resolved into their ultimate constituents in the laboratory with a view to detailed chemical investigation. It is not within the scope of this work to give a complete account of these operations, but it is desired to indicate the general lines upon which such an investigation of any natural fat or wax should be commenced. The extent to which the investigation is carried will depend on the technical processes for which the raw material is intended, and may proceed in some cases to exact research upon the constitution of the individual components by methods similar to those suggested in Chapters II. and III. of this

section ; whilst in others sufficient information for the purpose in hand will result from a more cursory examination.

The suggestions offered in this chapter will, it is believed, be of use as a general guide to the principles which may be followed in any particular instance.

Separation of Fats and Waxes into their Component Alcohols and Acids.—For the purpose in view it is recommended to effect saponification by means of alcoholic alkali. About 250–500 grms. of the raw material should be mixed with 4–8 times its weight of absolute alcohol, and about two-thirds of its weight of solid caustic soda or potash, and boiled vigorously under a good reflux condenser for 4 or 5 hours, at the end of which the alcohol should be distilled off as far as possible from a steam-bath. With very unsaturated fats, notably fish and similar oils, it is well to risk slightly incomplete saponification in preference to the danger of some isomerization or cyclization of the highly unsaturated constituents ; in such cases the amount of alkali may be reduced to about 20–25 per cent. of the weight of fat and the time of hydrolysis to 2 or 3 hours at most. In some instances, of course, much less fat may be available and it may be remarked that, if the fatty acids present are not too complex a mixture, the scheme of investigation here indicated can, if necessary, be carried through successfully with 100 g., or even 50 g., of original fat.

If there is no wax or unsaponifiable matter (hydrocarbon or sterol) present the removal of the alcohol may be continued under reduced pressure and the residual soap dissolved in water and acidified, leading to separation of the fatty acids, whilst glycerol, etc., remains in solution in the aqueous layer and may be recovered by evaporation and distillation if necessary.

If, however, there are appreciable amounts of "unsaponifiable matter" (wax alcohols, sterols, etc.) present, these should be removed by extraction with ether prior to proceeding further. To this end it is advisable only to distil off a portion of the alcohol from the saponified product, that

remaining assisting to prevent the undue formation of emulsions during the extraction with ether.

Extraction of relatively large volumes of soap solution in separating funnels is cumbersome and not too efficient, and the use of a continuous extraction apparatus is recommended for the purpose. Such an extractor may consist of a large bottle which is filled about two-thirds or three-quarters full with the aqueous-alcoholic soap solution. Ether is continuously distilled from a flask through a condenser attached above the bottle, whence it flows by a long vertical tube to near the bottom of the solution. A small stirrer slowly rotated on a long vertical shaft by a motor is also placed near the base of the solution. The ether droplets emerging from the tube pass up through the stirred soap solution and collect above it; the whole of the upper part of the bottle is originally filled with ether, which is then made to siphon back into the ether distillation flask. Use of this apparatus removes almost all the unsaponifiable matter usually encountered in any fatty material in the course of 24 hours' continuous operation. The combined ether extracts from the flask and the upper layer in the bottle are washed with water to remove traces of soaps and the non-fatty or "unsaponifiable" matter then recovered. The main soap solution and the washings mentioned are acidified and the fatty acids recovered by extraction with ether.

The original fat is thus resolved into (i) its component fatty acids, (ii) constituents soluble in water (usually only glycerol), and (iii) any non-fatty or unsaponifiable matter; each of these can then be examined separately.

Examination of Water-soluble Alcohols.—These are present in the acid aqueous extracts from the fatty acids, and in many cases consist only of glycerol. They may be recovered from the dilute aqueous solution by evaporating it, after exact neutralization with soda, until crystallization of the inorganic salts sets in; the residue is cooled, powdered up and ground with its own weight of anhydrous sodium sulphate in order to fix any uncombined

water. The powdered mixture of salts is then extracted in a Soxhlet apparatus for five hours with acetone, and the residue obtained after evaporation of the acetone is heated at 100° for one hour.

This residue may be fractionally distilled in vacuo in order to separate glycerol, trimethylene glycol, etc. In most cases glycerol is the only water-soluble alcohol present, and accordingly this section of the fat constituents is comparatively simple in type.

Examination of the Water-insoluble Neutral Materials.—These may consist of higher aliphatic alcohols, sterols, hydrocarbons, or a mixture of these substances. Except in rare cases, the proportion of sterols and hydrocarbons is very small, and large quantities of the original fat or wax must be worked up in order to obtain sufficient of these components for close examination. The methods available for their investigation are not systematized to any extent, and each case has to be considered more or less independently. Hydrocarbons may be separated to some extent by fractionation in a high vacuum, followed by crystallization from appropriate solvents. Sterols are most conveniently isolated in the form of their acetates, which lend themselves best to purification by fractional crystallization.

It should be mentioned that in some instances the principle of evaporative distillation (or the "molecular still") at extremely low pressures (0.001 mm.) has been found serviceable in the direct separation of unsaponifiable matter from fats. Sterols, vitamin-A, some hydrocarbons and similar bodies accompanying natural fats (including some of their breakdown products if oxidative rancidity has set in) can be conveniently removed by passage of a fat through the "molecular still" under suitable conditions. This has led to processes for the concentration of vitamins, etc., present in natural fats. It has also been used for the evaporation of non-polymerized from polymerized glycerides in the case of heat-polymerized unsaturated or "stand" oils (*cf.* Section VIII., Chapter I.).

The higher aliphatic alcohols which are found in quantity in sperm oils and certain waxes can frequently be separated from each other more or less completely by fractional distillation in vacuo (0·1-5 mm.), in the manner described below for the methyl or ethyl esters of the corresponding fatty acids. The individual alcohols, if solid (saturated), can usually be identified by their melting points or by the saponification equivalents and melting points of their acetates; the properties and constitutions of the unsaturated (liquid) alcohols of the same series are less well defined.

It should be mentioned that, if acetone is used to extract soap, a small amount of acetone condensation products formed in presence of free alkali will be found in this section of the products; these, however, are readily removed by distillation in steam.

Examination of the Fatty Acids.—The acidic components of the fats are those which generally receive most detailed attention, and somewhat fuller directions will therefore be given for the semi-quantitative separation of these compounds.

The most accurate, but somewhat tedious and prolonged, method available is to effect their quantitative separation by systematic fractional distillation of their methyl or ethyl esters.

This process was first suggested by Haller, who converted the glycerides directly into methyl esters by heating them with the equivalent amount of sodium methylate—a process which, however, is not capable of yielding accurate quantitative results.

It is advisable to proceed, as indicated above, to the isolation of the fatty acids, and then to combine the latter afresh with methyl or ethyl alcohol.

This plan also permits two groups of esters to be prepared, namely, those consisting mainly of the saturated and those consisting mainly of the unsaturated derivatives. The separate fractionation of the two groups of esters results in a simpler mixture being available in each case at the

distillation stage, and also avoids to a large extent the production of awkward "constant-boiling mixtures" of esters. For some reason unknown, a lower saturated ester (*e.g.* methyl palmitate) has a great tendency to form a specific component of constant boiling point with the next higher homologous oleic derivative (*e.g.* methyl oleate), whilst saturated and unsaturated esters of higher fatty acids of the same carbon atom content boil almost exactly at the same temperatures, and are therefore inseparable by fractional distillation.

The general scheme of treatment is therefore as follows :

- (i) Separation of the fatty acids into relatively saturated and unsaturated fractions.
- (ii) Fractional distillation of the esters of each of these two fractions of fatty acids.

(i) *Separation of the Saturated and Unsaturated Fatty Acids.*—The lead salts of most of the saturated fatty acids and of the solid unsaturated fatty acids are sparingly soluble in cold ether or alcohol, and this property is utilized for the present purpose.

The lead salt-ether method was introduced by Gusserow in 1828 and improved by Varrentrapp in 1840. This process (details of which have been given by Lewkowitsch and a full bibliography by Bertram) involves preliminary precipitation of the lead soaps from the aqueous alkali soap solutions and subsequent extraction of the washed precipitated lead soaps with ether. It has been largely superseded in ordinary analytical practice by separation of the lead salts from alcohol, instead of ether, an alternative first suggested by Twitchell in 1921.

A convenient modification of the Twitchell procedure, applicable to the comparatively large amounts of fatty acids involved in detailed quantitative work, is as follows : The mixed fatty acids (*e.g.* 200 g.) are dissolved in 95 per cent. alcohol (1000 c.c.), the solution is boiled and mixed with a boiling solution of lead acetate (140 g.) in 95 per cent. alcohol (1000 c.c., containing 15 g. of glacial acetic

acid). The lead salts deposited on cooling overnight at 15° are recrystallized from alcohol (2000 c.c., containing 15 g. of glacial acetic acid), the "solid" acids are regenerated from the recrystallized lead salts, and the "liquid" acids recovered from the mixed alcoholic filtrates from both operations. (For fuller working details, the original literature or larger monographs may be consulted.)

Some idea of the separation effected by the process described above may be gained from the following relative data as to the solubility of lead salts in cold 95 per cent. alcohol :

Saturated acids.	Unsaturated acids.
Lead butyrate, caproate, caprylate —Soluble.	
Lead caprate, laurate—Fairly soluble.	
Lead myristate—Distinctly soluble..	Lead myristoleate—Very soluble.
Lead palmitate—Almost insoluble ..	Lead palmitoleate—Freely soluble.
Lead stearate—Almost insoluble ..	Lead oleate—Soluble.
	Lead elaidate, iso-oleate—Spar-
	ingly soluble.
	Lead linoleate and linolenate—
	Freely soluble.
Lead arachidate—Insoluble ..	Lead gadoleate—Sparingly soluble.
Lead behenate—Insoluble ..	Lead erucate — Only slightly soluble.
	Lead salts of highly unsaturated C_{18} and C_{22} acids—Freely sol- uble.

(ii) *Fractional Distillation of the Fatty Acid Esters.*—Each of the fractions of the fatty acids resulting from the lead salt separation is converted to methyl or ethyl esters by dissolving in about four times its weight of the alcohol (to which 2 per cent. of concentrated sulphuric acid is added), and boiling under reflux for about two hours. Esterification proceeds very readily and almost to completion, and, after removal of as much alcohol as possible by distillation on a water-bath, the residue is dissolved in ether and washed, first with water to remove mineral acid, and then cautiously with dilute sodium carbonate in order to remove unchanged fatty acid with as little formation of soap-ether emulsion as possible.

The crude dried neutral esters, after removal of ether, are distilled slowly in a fractional distillation apparatus under a pressure of 0.1-1 mm. (produced by a good modern rotary oil-pump). The fractionation apparatus may consist simply of a Willstätter bulb (containing two globular extensions between the bulb itself and the side-arm of the flask, the lower one of which is more than half filled with thin metal or glass rings); in this case adequate separation is rarely effected in one distillation and the first series of fractions normally each require a further refractionation in order to provide ester fractions of a sufficient degree of simplicity. Of recent years, the use of more elaborate, electrically heated columns has been introduced in work of this kind. A very useful type has been described by Longenecker (1937); it comprises a column about 90 cm. high made up of three concentric glass tubes. The inner tube (17 mm. diam.) is surrounded by another (25 mm. diam.) around which nichrome wire is wound and carries an electric current which can be suitably regulated by external fixed and variable resistances. The heating jacket is protected by an outer tube (33 mm. diam.). The inner tube is packed for a distance of 60 cm. with glass helices. At the top of the column the vapours pass to a simple reflux condenser, the condensate being partly or wholly returnable to the column or withdrawn to a receiver by means of a stopcock. With an apparatus of this type a single distillation is sufficient, and usually occupies 5-7 hours, according to the quantity of esters distilled. Much sharper separation is obtained than with the simpler Willstätter bulb.

Here again, the reader who requires fuller working details of the ester-fractionation technique, and of the methods of calculation subsequently involved, must be referred to the original papers or to the author's "Chemical Constitution of Natural Fats" (Chapter XI.).

The actual boiling points at the head of the columns are not very significant, although useful as a guide to the course of the fractionation in any given instance; but it may be mentioned that, with a vacuum of about 0.2 mm., the

boiling points (or, rather, column head temperatures) of typical methyl esters are approximately as follows : laurate 83-87°, myristate 95-100°, palmitate 120-125°, stearate or oleate 135-140°.

Throughout the work the saponification equivalent and the iodine absorption of each fraction of ester or of fatty acid is determined, but correspondence of the saponification equivalent of a main fraction with that of a specific ester does not of itself indicate the presence of the individual suspected : for example, an equivalent of 298 is given by either methyl stearate or an equimolecular mixture of methyl palmitate, stearate and arachidate, or by other mixtures of more complex nature, and these may quite possibly be encountered. It is necessary to confirm the individuality of each main fraction by definite characterization (for example, the melting point of the ester or corresponding acid, if solid ; or of a hydroxy-oxidation product, in the case of the ester of a liquid unsaturated acid).

The primary object of the process is to ensure that, within very narrow limits, each ester fraction contains mixtures of not more than two saturated esters, and not more than two homologous groups of unsaturated esters. When this has been achieved, it leads to the following results :

(i) Individual esters may be examined with reference to their chemical structure.

(ii) If the whole series of operations has been conducted on a quantitative basis, the weights having been recorded at each stage of each operation and analytical determinations of molecular magnitude and degree of unsaturation having been systematically made, it is possible, when the individual nature of the main fractions has been established, to calculate the approximate percentage composition of the fatty acids present in the original fat or wax with considerable accuracy. To obtain accurate results the process must be carried out on somewhat large quantities of fat. If the component acids are comparatively few in number (not more than five or six) 100-150 grams of fat will suffice ; in the rare cases in which a fat contains only two or three

component acids, even 20–30 grams is adequate; but in fats such as butter, fish oils, etc., where the number of component acids is very much greater, 250 grams or still more should be employed when possible.

Examples of natural fatty acid mixtures which have been studied by this means will be found in the tables given in Section II., Chapter III.

Separation of Oleic Acid from more Unsaturated Acids.—This may be partially effected by crystallization of the lithium salts of the mixed unsaturated acids from 80 per cent. alcohol, or of the barium salts from a mixture of moist benzol and alcohol. Either of these methods yields oleic acid practically free from less saturated acids (*e.g.* linoleic), but does not serve for the isolation of the latter in a pure condition, since a considerable proportion of the metallic oleate is always left in the mother liquors.

An alternative method now available for the separation of oleic acid is its crystallization from acetone at temperatures considerably below 0°, due originally to J. B. Brown and collaborators. The acetone solution may be cooled in an external bath of solid carbon dioxide or solid carbon dioxide in acetone, or the acetone solution itself may be cooled by direct addition of solid carbon dioxide.

For example, the acids from olive oil (the most convenient source of oleic acid) are first freed from saturated acids as far as possible by depositing the latter from acetone at -20°, followed by several crystallizations of the oleic acid from about 7 per cent. solution in acetone at -60°. About 50 per cent. of the oleic acid present in olive oil can thus be recovered free from linoleic acid; to obtain complete purity, it (*or its ester*) should then be fractionally distilled to remove the last traces of palmitic acid.

Similarly, linoleic acid of over 90 per cent. purity (the balance being oleic acid) has been prepared by crystallizing maize oil acids from acetone, first at -20° and then at -50° to remove successively saturated and the bulk of the oleic acid present, and finally several times at -70°.

Linolenic acid has been obtained as a concentrate of

about 85 per cent. linolenic and 15 per cent. linoleic acid by similar treatment of the mixed acids of linseed or perilla oil, followed by final recrystallizations of the product (separated from acetone at -75°) from dilute solutions in light petroleum at -55° to -65° .

Examination of Mixed Glycerides present in Natural Fats.—Much painstaking and careful research by several workers from about 1895 onwards showed that, except in a few special instances, physical methods of separation are incapable of giving more than, at best, a very partial separation of the mixture of mixed triglycerides in a natural fat into a number of somewhat simpler mixtures. The chief contribution of these attempts to resolve fats into their constituent glycerides by crystallization (or, occasionally, distillation in a very high vacuum) is the strong presumptive evidence that for the most part the triglycerides in natural fats are mixed, and not simple, in character. From 1927 onwards chemical methods of investigation have been applied in conjunction with the physical methods, and a good deal of qualitative knowledge of the component glycerides in many natural fats has been acquired. The precision of the quantitative data on glycerides does not reach that now attained in our knowledge of the component acids of the fats, but it has proved sufficient to indicate the main characteristics of glyceride structure (or the assemblage of fatty acids, three at a time, into molecules of triglycerides) in the natural fats. It is indeed now possible in most cases, with some confidence, to predict the chief component glycerides and their proportions in many natural fats when the proportions of the major component acids present are known.

Probably the most useful asset in the investigation of the component glycerides of fats has been the quantitative isolation and study of any triglycerides present which contain three saturated acyl groups ("fully saturated glycerides"). This technique was originated by Hilditch and Lea in 1927 and has since been applied to many fats. It was at once discovered that in many cases, especially in seed fats, little or no fully saturated components appeared

unless saturated acids formed two-thirds or more of the mixed fatty acids, whilst beyond this point the amount of fully saturated glycerides was such that maximum proportions of glycerides containing saturated and unsaturated acids in the average "association ratio" of 1·5 mol. of the former to 1 mol. of the latter were present. In specific groups of fats (animal depot fats rich in stearic acid, and milk fats rich in lower saturated acids), however, a departure from this generalization was evident, the proportions of fully saturated glycerides being greater, for a given ratio of saturated to unsaturated acids in the whole fat, than in the typical cases mentioned.

In many fats, notably liquid seed fats, the major component acids are oleic and linoleic, with subordinate amounts of saturated acids, usually mainly palmitic. Here a different method of attack is necessary : study of completely or partly hydrogenated fats of this nature, in which the tristearin produced by saturation of oleo- or linoleo-glycerides can be approximately, though not precisely, estimated, affords a means of "sorting" the fat glycerides into tri-C₁₈ glycerides and those containing both C₁₈ and non-C₁₈ acyl groups. Again, the content of tri-C₁₈ glycerides in such cases usually approaches the minimum proportion consistent with the composition of the mixed acids.

Latterly, the precision of glyceride structure determinations has been increased, in cases of solid or semi-solid fats, by first resolving them into simpler mixtures of mixed triglycerides by systematic crystallization from acetone at 0° or higher ; whilst a similar method has been developed for liquid fats by crystallization from acetone and solid carbon dioxide at progressively lowered temperatures down to about -40°. By determining the component acids present in each fat-fraction so obtained, by isolating fully saturated glycerides where present or by estimating tristearin content after hydrogenation of specific fractions, and by again, when necessary, resolving the fully saturated or hydrogenated fractions by further crystallizations from acetone, ether, etc., coupled with component acid deter-

minations on the fully saturated or hydrogenated sub-fractions finally obtained, it has proved possible in many instances to arrive at a fairly close estimate of the various mixed glycerides of which a natural fat is composed.

The component glycerides of a number of specific fats, as indicated by investigations of the nature discussed above, are referred to in Section II., Chapters II. and III. ; at this point it will suffice to give a very brief general discussion of glyceride structure in natural fats. Whereas the component acids present in a fat seem to depend on very specific considerations and, especially, to be closely connected with biological or species differences, these acids—irrespective of the source of a fat, vegetable or animal, land or aquatic, or of the particular mixture of acids present in any given case—seem to be woven into molecules of triglycerides on one main principle, namely, that nature strongly favours the elaboration of mixed, and not simple, triglycerides. This connotes that the various acids are, as it were, distributed very evenly, on the whole, amongst the glycerol molecules, and has led to the phenomenon being called the “rule of even distribution.” The consequence of this is that any individual triglyceride molecule tends towards maximum heterogeneity in its composition. Concurrently, if paradoxically, in a few special instances it also leads to the production of a few natural fats which approach much more closely than usual to the case of a homogeneous chemical compound ; in cacao butter, for instance, with large and not far from equivalent proportions of palmitic, stearic and oleic acids, much of the material consists of oleopalmitostearin.

This principle of “even distribution” is closely followed in practically all vegetable seed fats and many fruit-coat fats, in the fats of aquatic plant and animal life (including both fishes and marine mammals), and in those of land animals and birds in many cases. As already stated, however, there are apparent exceptions (now seen to be probably superimposed modifications on the “even distribution” principle) in the cases of animal depot fats, such as tallow, which are relatively rich in stearic acid, and of animal milk fats, which

include about 20–25 per cent. of saturated acids of lower molecular weight than palmitic acid in their component acids. Broadly speaking, in all such instances so far studied, the proportion of stearic acid or of lower saturated acids (as the case may be) seems to be closely connected with that of the oleic acid present, the sum of the latter and either of the former being of an approximately constant order. It is therefore at present supposed that both these modifications may arise by further modification of a pre-formed mixture of palmitodioleo- and similar glycerides built upon the usual heterogeneous principle. Partial saturation of such oleo-glycerides in the case of the depot fats, and transformation of such oleo-glycerides (by processes involving shortening of the oleic chain) in the case of the milk fats, would account for the observed composition of the glycerides in these two classes of fats. It may be added that there is considerable evidence that both saturation (hydrogenation) and desaturation (dehydrogenation) of fats can proceed in the living organism, whilst studies of Schoenheimer and Rittenberg based on the administration to animals of fatty compounds containing deuterium ("heavy hydrogen"), such as deuterostearates and deuteropalmitates, point to the likelihood that the higher fatty acyl chains can be lengthened or shortened, two carbon atoms at a time, prior to storage as depot fats.

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SECTION II.—THE COMPOSITION OF FATS OCCURRING IN NATURE

CHAPTER I.—GENERAL DISTRIBUTION AND OUTPUT IN NATURE OF THE FATS AND WAXES

THE quantity of fats and waxes produced in nature each year is enormous in the aggregate, and yet is capable of being increased in many directions by the more intensive culture of plants and animals which yield serviceable varieties of these compounds.

Waxes.—The waxes are subordinate in technical importance to the fats, and may be considered briefly before considering the latter group. Most of the waxes are of the nature of annual crops, since they are produced either on the leaves or berries of plants or by secretions of insects ; the spermaceti waxes, however, require an uncertain number of years for production (the time required by sperm whales to attain maturity is not yet known). Taken as a whole, it may be said that waxes, animal and vegetable, are indigenous to all climates ; those which find technical application, however, are mainly tropical and sub-tropical vegetable products. At the same time it must be pointed out that beeswax comes from all over the world, whilst of the vegetable waxes, those from flax and other similar plants develop in temperate climates. The composition of the waxes is more varied than that of the fats and, at present, less investigated ; consequently it is not possible to discuss them so thoroughly as the fats from the standpoint of correlation of constitution and distribution, etc., nor indeed

is it so necessary, in view of their relatively minor application in the arts.

Fats, Liquid and Solid.—The development of various typical kinds of fats can be connected to a certain, and sometimes to a notable, extent with the conditions under which their parent plants or animals live.

If we consider in the first place the natural output of the fats which find general application, it is evident that the period required for the production of fats varies from a few hours to several years.

The most rapid output, of course, is that of the milk fats or animal butters, which are produced continuously during the lactation period. Apart from these, the most rapid yields of fat obtain in the vegetable kingdom, where almost without exception fruits or seeds mature annually.

In the case of annuals such as the flax, cotton, sunflower or soya bean plants the life-cycle of the plant is complete within a few months, and it may even be possible to secure two crops per year from the same area in some cases. Further, with a number of seeds such as flax or soya beans which are grown in the Northern and Southern hemispheres and in sub-tropical as well as temperate climates, crops are ripening throughout the world at different periods of the year and are thus available for oil extraction, say, in England, practically continuously.

Many important vegetable fats, however, are extracted from the fruits of perennial shrubs or trees such as the olive, oil palm, or coconut palm, to name only three familiar instances. Here a period of a few years, not exceeding ten as a rule, elapses before a young tree commences to bear fruit regularly and profitably, but after this an annual crop is usually obtained over a long period of years before the plant becomes unfruitful by reason of old age.

The utilization of animal fats other than milk fats involves, of course, the death of the animal concerned and the time required to obtain a "crop" is thus determined by the period of growth of the animals.

Pigs, sheep, and cattle come to maturity in the course

of from one to three or four years, and on an average the former may perhaps require from one to two years, and sheep and cattle from two to four years, before their fat content is at a maximum economic value.

The maturing period of marine animals is much less certain. Small fish of the herring, sardine, and menhaden types are of rapid growth, whilst cod, rays, and the smaller sharks probably require a few years in which to come to full size; the growth of larger marine animals of the mammalian type, including seals and especially whales, is, however, a much less certain factor. It is evident that a whale requires a considerable time to approach maturity, and some apprehension is felt at the rate at which whales have been caught during the past thirty years in order to meet the demand for hydrogenated whale oil. A systematic marine investigation of the habits and life-cycle of the common whales has been undertaken in order to obtain information as to the period of growth and the rate of reproduction of whales, and attempts have been made to control the whaling industry from this point of view in order to guard against risk of extermination of the more valuable oil-bearing species.

Another factor which has some bearing on the output of natural fats is the extent to which other parts of the source of fat have economic value.

Thus the coconut palm, as is well known, yields from the exterior of the nuts the coconut fibre which is valuable for matting, etc., and also coconut "milk" and other products; a similar case is that of rubber seed oil from *Hevea brasiliensis*, the source of plantation rubber, and it is probable that increasingly large quantities of this oil will become available as a by-product of the plantation rubber industry. The cacao bean, yielding cocoa as well as cacao butter, is another instance.

Amongst temperate or sub-tropical plants, again, we may note the high food value of the soya bean, and the textile fibres which are the basis of the flax- (linseed) and cotton-growing branches of agriculture. In both these

cases, and in the case of maize, which is primarily grown as a food and a source of glucose, the fatty oils, although in themselves the raw materials of important industries, are essentially of the nature of by-products ; it should be noted, however, that the care taken to fix the strain of seed in order to obtain consistent quality in the fibre, etc., has the further effect of producing a remarkably constant composition in the fats obtained in commerce from such sources.

Pigs and cattle (including sheep) are of course reared as much or more for consumption as flesh than for the sake of the lard, tallow, etc., obtainable therefrom. Sheep have in addition the textile interests due to the wool, and here again it may be observed that a by-product of the wool itself, which must be removed prior to weaving, is the wool fat or wool grease ; this material is therefore available in very large quantities, but owing to its crude nature as at present extracted it lacks profitable outlets to a large extent. The production of glue is also to be borne in mind in connection with cattle.

Many of the fish, such as cod, herrings, or sardines, are valued as food equally or more than for their fatty oils, whilst seals are primarily sought for their skins, and whales, in addition to the oil, furnish whale ivory, whalebone and, occasionally, ambergris, and may eventually prove to be a valuable source of gelatine and glue.

The economic extraction of fats has therefore to be considered in conjunction with a variety of other circumstances, not the least important of which is the utility of the non-fatty portions of the plant or animal which is the source of the fatty material.

General Distribution of Fats and Waxes. I. Vegetable Fats.—The production of vegetable fats may be considered in relation to climatic conditions as follows :

(i) *Tropical Countries.*—Important fats of tropical vegetation are those from the seeds or kernels of tropical forest trees and shrubs which, as shown in Chapter III. of this section, are notable for their low content of unsaturated

acids, and their relatively abundant content of fatty acids containing less than 16 carbon atoms in the molecule. Other tropical fats, including palm oil, cacao butter, Japan wax, shea, Kokum, and Baku butters, do not contain any quantity of acids of lower molecular weight than palmitic acid, $C_{16}H_{32}O_2$, but by reason of the preponderance of this and stearic acid over the oleic acid present they belong in all cases to the class of solid, and not liquid, fats.

There are, nevertheless, certain more unsaturated and therefore liquid fats produced in the seeds of some species of tropical plants. Amongst these may be mentioned groundnut, kapok, croton and chaulmoogra oils, argemone, rubber seed, tung, oiticica and candlenut oils, the latter being "drying" or relatively unsaturated fats with iodine absorptions of 120–160.

On the whole, however, saturated fatty acids are more prominent in the fats produced from seeds and fruits of tropical plants than in vegetable fats from cooler climates.

(ii) *Sub-tropical Climates*.—Few, if any, solid vegetable fats are produced other than in the tropical zones, although it must be remarked that this does not apply to plant waxes. Cottonseed wax, for example, is a sub-tropical product, and flax and esparto wax of temperate or sub-tropical origin, whilst the carnauba and candelilla waxes of Brazil, Mexico, and Texas probably do not require absolutely tropical conditions of growth.

So far as fats are concerned, the sub-tropical flora tends mainly to produce liquid fats of the "non-drying" or "semi-drying" type. Amongst the former may be noted olive, almond, and rice oils, and amongst the latter cotton-seed, sesame, maize, and sunflower seed oils (the latter, however, also matures in many temperate climates). Rather more of the highly unsaturated or "drying" oils occur in sub-tropical than in tropical areas, for example, soya bean, safflower, hemp seed, poppy seed, stillingia, perilla, and China wood (tung) oils, but a number of these are also grown successfully in the cooler temperate zones.

(iii) *Temperate Climates*.—The tendency of the fats from

temperate vegetation is towards still greater unsaturation than in the preceding cases. Almost the only notable representatives of the "non-drying" or olein group of fatty oils are the rape and mustard seed oils of various *Brassica* and allied species ; these, however, contain fair proportions of linolein as well as olein and are further characterized by the presence of the glyceride of erucic acid, an acid of the C₂₂ series which, like oleic acid, is monoethylenic.

Wheat oil and sunflower seed oil represent "semi-drying" fatty oils of temperate origin, but many other temperate vegetable fats are "drying" oils of iodine absorption 130-180, such as soya bean, hemp seed, walnut, and linseed oil.

II. *Animal Fats*.—It is not possible to draw any similar simple distinction between climatic conditions and the character of animal fats for the following reasons :

(a) The animal fats obtained in commerce are drawn from a much more restricted range of species than in the vegetable kingdom, and the main types cultivated (*i.e.* domestic animals) are grown in a variety of climates.

(b) The nature of animal fat is not so constant as that from vegetable sources, since it is dependent to some extent on the fat ingested as food and also on the habit of the animal, whether comparatively free or confined. Animals held in close captivity produce harder, less unsaturated fat than the corresponding wild or semi-wild beasts.

The only generalities worth recording are that the milk fats of many animals, whilst revealing minor differences in characteristics, are broadly similar in type and are almost invariably distinguished from all other fats, vegetable or animal, by containing a small but definite percentage of combined butyric and caproic (caprylic, capric) acids ; and that lards and tallow from pigs, cattle, and sheep, whether bred in England, Canada, Australia, or the somewhat warmer climates of South America, are also broadly similar in type, but subject to minor variations which are usually more comparable with differences in diet than in climate.

On the other hand, all fish oils, whether from Arctic, temperate, or warmer seas, seem to be characterized by the presence of a greater or less proportion (i) of glycerides of very highly unsaturated acids containing 20 and 22 carbon atoms per molecule, and (ii) of glycerides of hexadecenoic acid, $C_{16}H_{30}O_2$, a peculiarity which they share with the fatty oils of the whale and other marine mammals.

Whale oil fatty acids, again, are apparently similar in type independently of the cold or warm origin of the animal (*cf.* p. 174); a most interesting but quite unexplained problem in connection with the genesis of fatty matter in the whale is why the sperm whale, which inhabits the same waters as the other whales (such as the Greenland, Finner, or South Sea), should have much of its fatty acids combined with higher fatty alcohols, instead of with glycerol, whereas the other species contain the fatty acids exclusively as glycerides, following the more customary rule.

It will be inferred from what has been stated that much work of a biochemical nature remains to be done before any systematic generalization can be arrived at as to the effect of species, habitat, climate, etc., on the production and composition of animal fats.

Classification of Fats and Waxes used in Industry.—In accordance with the facts outlined above as to the output and distribution of natural fats, those members of the group which are utilized to any extent in industry will be discussed in some detail in the next chapter in the order given below.

It may be pointed out that well over a thousand fats and waxes, vegetable and animal, have been definitely characterized, of which about eighty or ninety are in sufficient technical use to demand inclusion in this book. The reader who desires to obtain particulars of the less commonly used fats and waxes is recommended to refer to Lewkowitsch's *Manual on Oils, Fats, and Waxes*, volume ii., chapter xiv., Halden and Grün's *Analyse der Fette und Wachse*, volume ii. (1929), Jamieson's *Vegetable Fats and Oils* (1932), or the author's *Chemical Constitution of Natural Fats* (1940).

The fats and waxes referred to in the present book are grouped as follows :

VEGETABLE FATS.

- I. *Solid Fats : The vegetable butter group, including the nut oils.*
Coconut oil, palm kernel and palm oil, cohune oil, babassu fat.
Cacao butter, Chinese vegetable tallow, Borneo tallow (Illipé).
Nutmeg butter, Japan wax.
Mowrah butter; shea butter; *Allanblackia* fats, etc.
- II. *Liquid Fats : The "non-drying" vegetable oils.*
Olive oil and olive kernel oil.
Groundnut (*arachis*) oil.
Almond, apricot kernel, peach kernel, plum kernel oils.
Rice oil.
Castor oil.
Rape, ravigon and Jamba rape oils.
Black and white mustard-seed oils.
- III. *Liquid Fats : The "semi-drying" vegetable oils.*
Cottonseed, kapok, sesame, maize, wheat, sunflower-seed oils.
Croton oil.
- IV. *Liquid Fats : The "drying" vegetable oils.*
Soya bean, safflower, argemone, hemp seed, walnut, poppy seed, rubber seed, candlenut, stillingia, perilla, China wood (tung), oiticica and linseed oils.
- V. *Solid Fats : Chaulmoogra oil group.*
Chaulmoogra, hydnocarpus, and lukrabo oils.

ANIMAL FATS.

- I. *Solid Fats : Butter Fats.*
(Cow) Butter; Ghee (cow or buffalo) butter, goat, sheep, and reindeer butter.
- II. *Solid Fats : Domestic Mammalian Body Fats.*
Lard, skin grease.
Beef and mutton tallow.
Bone fat, wool fat, or wool grease.
- III. *Liquid Fats : Domestic Mammalian Foot oils.*
Neat's foot oil.
- IV. *Liquid Fats : Marine Animal oils : (a) Fish oils.*
Cod liver and cod oil.
Herring, salmon, sardine, Jap fish and menhaden oils.
Shark, dogfish and ray oils.
- V. *Liquid Fats : Marine Animal Oils : (b) Mammalian oils.*
Whale oils.
Seal oil.
Dolphin and porpoise oils.

WAXES.

- I. *Vegetable.*
Carnauba, candelilla (Montan), flax, cottonseed, seaweed waxes.
- II. *Insect.*
Beeswax; Chinese insect wax.
- III. *Marine Animal (*Spermaceti*).*
Sperm whale oil; arctic sperm oil.

CHAPTER II.—SOME OF THE MORE COMMONLY OCCURRING AND TECHNICALLY USEFUL FATS AND WAXES

THIS chapter is devoted to a very condensed summary of the individual varieties of fats and waxes which at present most frequently find application in industry. Whilst the more important members are also dealt with separately, the main characteristics of each group are collected together in tables, following the classification at the end of the previous chapter.

Each table consists of two divisions :—

i. The first gives the commercial name or names of the fat, the species from which it is derived and the districts in which the latter is most largely grown for the purpose of fat extraction ; the names of the most important technical fats are given in capitals.

The figures relating to production are of a very indefinite character : they have been added merely in order to give some idea of the relative proportions of the industry. In consequence of variability in crop yield and incomplete statistical information it is not possible to give more than a relative indication of the magnitude of the industry. The data, which represent tons per annum of crude fat as it comes on the market, are given when possible in the form of an estimate of the world production and of the annual imports into the United Kingdom.

The fats and waxes included in the tables are, primarily, those at present largely employed for the purposes indicated in the final columns and, in addition, those which occur in sufficient abundance and are so constituted that they might well supplement existing sources of supply under suitable economic conditions.

2. The second table in each division deals with the main analytical data by which the fats are assessed for commercial purposes. This consists of two sections, corresponding to the classes of data which Lewkowitsch has termed "characteristics" and "variables."

The *characteristics* of fats and waxes as obtained in the market are by no means constant in many cases, and it is therefore necessary to quote a range of values which covers the variation normally met with in samples of reasonable quality.

The *variables* noted are the *free acidity* and the amount of *unsaponifiable matter*.

Except in the case of the waxes (where the "unsaponifiable matter" as determined includes the higher fatty alcoholic constituents of the original wax ester), the latter value should be small and is largely dependent on the efficiency of the method of extraction employed (*cf.* Section III., Chapter I.).

Again, free acidity is mainly conditioned by the mode of gathering, storage, and extraction of the fat or wax ; where modern processes are employed on a sufficiently large scale, the free acidity is usually of a low order, but under less hygienic conditions it may vary upwards within wide limits.

The methods employed in the determination of the values included in these tables have been discussed in Section I. (Chapter IV.), and it is only necessary here to add the following notes :

The *specific gravity* is given where possible for a temperature of 15° C. ; in the case of solid fats and waxes the density is determined in the liquid state and must therefore be measured at higher temperatures, *e.g.* 40° or 60° C.

The *refractive index* is given as such, rather than in oleo- or butyro-refractometric degrees ; tables correlating the latter values with the index of refraction will be found on p. 78.

The *setting point* and *melting point of fats* are characteristics of a somewhat indefinite nature and in general are not

of great utility; the setting point should be determined, where necessary, by the standard "titer" method (p. 73).

The corresponding values for the *combined fatty acids* afford, as a rule, a much clearer guide to the nature of the fat under examination.

The *saponification value* and *saponification equivalent* (cf. p. 40) are both given; whilst the *saponification value* is a convenient criterion in the case of fats containing large and variable amounts of true unsaponifiable matter or free acidity, the *saponification equivalent* gives a clearer indication of the mean molecular magnitude of the glycerides or wax esters in fats or waxes which are almost exclusively composed of these respective classes of esters.

The *iodine absorption* is one of the most characteristic and important properties of fats and waxes, and indicates the average state of unsaturation of the material.

The *Reichert-Meissl value*, indicating the proportion of acids volatile in steam, and the *acetyl value*, indicating the proportion of hydroxylated compounds, are only given in the cases where they are of particular use.

The subsequent notes on the various fats are intended mainly to focus the reader's attention on their chief specific utility in the various industries, their accessibility in nature and relative ease of production, the value of the resulting residual seed-meal or cake as by-product, etc. To do this it is necessary in some cases to refer more or less in detail to the chemical components of the fats in question, but systematic treatment of the composition of the fats enumerated is deferred until the succeeding chapter. Again, except in a few of the more obvious instances, the fats have been considered with reference to their use as extracted, and not as they may be modified by partial hydrogenation. Most of the commoner fats have in addition received attention at one time or another with reference to their industrial values after hydrogenation to various degrees, but this aspect of the subject will be dealt with in the chapter on Fat-hydrogenation (Section III., Chapter III.).

I. Solid Fats.—The Vegetable Butter Group, including the Nut Oils.
 (i.) *Occurrence.*

Fat.	Source.	Habitat.	Approximate annual		Technical applications.	Fat-content.
			Production.	Imports to U.K.		
COCONUT OIL ..	Cocos nucifera and C. butyracea (Coconuts). <i>Elaeis guineensis</i> <i>vars.</i>	Southern Tropical Islands and Brazil.	Tons. 500,000- 650,000	Tons. 80,000- 100,000	Vegetable butters; high class soaps.	63-65% dried copra.
PALM KERNEL OIL ..	West Africa (Gold Coast, Nigeria, Congo, etc.). Malaya and Dutch East Indies.	West Africa (Gold Coast, Nigeria, Congo, etc.). Malaya and Dutch East Indies.	{ 225,000- 275,000 300,000- 400,000	{ 60,000- 70,000 80,000- 100,000	As coconut oil. Soft edible fats; soaps.	45-50% (kernel). 30-60% (fruit pulp).
PALM OIL ..	Central America ..	Central America ..	Growing.	—	Edible fats.	65-70% (kernel). 36-42% (kernel). 63-70% (kernel).
Cohune oil ..	Brazil ..	Brazil ..	—	—	Confectionery fat.	50-55% (beans).
Murumuru fat ..	Astrocaryum murumuru ..	Brazil ..	—	—	Cacao butter substitute.	20-30% (seeds).
Babassu fat ..	Attalea cohune ..	Brazil ..	—	—	Cacao butter substitute.	45-50% (nuts).
CACAO BUTTER ..	Theobroma cacao ..	West Indies, Central and South America, W. Africa.	100,000	40,000- 50,000	Confectionery fat.	40% (seeds).
Chinese vegetable tallow.	Stillingia sebifera.	China, also India ..	Ca. 7000- 10,000	—	Pharmacy (ointments), Polishes.	20-30% (berries).
Borneo tallow	Shorea species ..	Malaya and Borneo ..	—	—	—	50-55% (seed).
Nutmeg butter ..	Myristica officinalis.	East Indies ..	Ca. 500	1000-2000	Pharmacy (ointments), Polishes.	50% (kernels).
Japan wax ..	Rhus species ..	China, India, Japan ..	Ca. 4000	—	—	—
Mowrah butter ..	Bassia latifolia ..	Northern India, E. Indies, Sudan and West Africa.	50,000-100,000	—	—	—
Shea butter ..	Butyrospermum Parkii	West Africa.	—	—	—	—
Mkanyi tallow ..	Allanblackia sp.	—	—	—	—	—

(iii.) Average Analytical Characteristics.

Fat.	Sp. gr. (water at 15°).	Ref. index.	Setting pt.	M. pt.	Sap. Val.	Sap. Eq.	Iodine absn. %	Combined fatty acids Titer.	Free fatty acids,		% Unsap.
									°C.	°C.	
COCONUT OIL ..	0·926/15°	1·443/60°	19-23°	24-28°	250-260	216-225	8-10	20-22°	24-27°	5-13	2-5% ^a
	0·874/99°	1·443/60°	19-24°	25-30°	243-250	225-230	15-18	20-25°	25-28.5°	5-20	2-7% ^b
PALM KERNEL OIL ..	0·930/15°	1·443/60°	31-39°	27-30°	196-210	256-285	51-58	36-45°	44-50°	10-60	4-27% ^c
PALM OIL ..	0·921-	1·451/60°									0·3-0·6%
Cohune oil ..	0·925/15°	1·450/40°	15-16°	18-24°	252-256	219-223	11-14	19-21°	27-30°	1-20	0·4-7% ^d
	0·868/100°	1·450/40°	30-32°	34-35°	237-242	231-237	11-12	26°	30°	1-3	0·4-1% ^e
Murumuru fat ..	0·920/15°	1·452/40°	22-23°	22-26°	247-253	221-227	12-16	23-24°	25°	6	0·6% ^f
Babassu fat ..	0·869/100°	1·449/40°									0·5%
CACAO BUTTER ..	0·970/15°	1·450/60°	23-26°	33-35°	192-195	286-292	35-42	48-50°	48-53°	1-3	0·5-1·5% ^g
Chinese vegetable tallow ..	0·858/98°										0·3-0·8%
Borneo tallow ..	0·920/15°	1·451/60°	25-35°	43-46°	200-203	276-280	28-38	52-53°	53-57°	2-14	1-7% ^h
	0·856/100°	1·456/40°	22-30°	28-37°	192-196	285-292	30-33	50-54°	52-57°	8-30	variable up to 1%
Nutmeg butter ..	0·959/15°	1·470/40°	41-44°	43-48°	172-179	313-326	48-52	40-45°	40-50°	11-14	4-6% ⁱ
Japan wax ..	0·990/15°	—	48-50°	50-56°	220-237	237-255	8-10	58-59°	54-62°	7-13	3-15% ^j
Mowrah butter ..	0·920/15°	1·460/40°	18-25°	23-31°	187-194	289-299	58-63	38-40°	39-45°	5-40	3-20% ^k
Shea butter ..	0·917/15°	1·463/40°	17-27°	23-32°	186-196	286-302	56-62	48-53°	51-56°	4-30	2-15% ^l
<i>Allanblackia</i> sp.	0·939/15°	1·458/40°	30-38°	40-45°	187-192	292-300	38-44	57-61°	59-62°	2-20	3-10% ^m
										1-10% ⁿ	up to 1%

^a Calculated as palmitic acid.

^b Acetyl value about 30.

^c Calculated as lauric acid.

^d Calculated as myristic acid.

^e Calculated as oleic acid.

^f Calculated as stearic acid.

^g Calculated as behenic acid.

^h Calculated as arachidic acid.

ⁱ Calculated as linoleic acid.

^j Calculated as behenic acid.

^k Calculated as behenic acid.

^l Calculated as behenic acid.

^m Calculated as behenic acid.

ⁿ Calculated as behenic acid.

VEGETABLE FATS

**I. Solid Fats. The Vegetable Butter Group,
including the Nut Oils.**

This group of fats is of great importance by reason of the fact that it is a source of the best qualities of edible solid vegetable fats and also of toilet soaps. This is owing to the presence in the fats of large proportions of the glycerides of lauric, myristic, and palmitic acids, in consequence of which, on the one hand, the consistency of the fats is ideal for many edible products, and on the other hand, the solubility, hardness, and detergent power of the corresponding soaps are at a maximum. Their composition varies widely according to the genus and even the species of the fruit ; this will be noticed in the few examples which are dealt with here and which form but a small proportion of the fats which are known to be produced in the abundant and varied tropical flora. The variations in chemical composition receive further attention in the next chapter.

Coconut Oil.—The coconut palm (*Cocos nucifera*) grows on or near the coastline of the Atlantic and Pacific tropical seas. The bulk of the coconut oil produced comes from the Pacific seaboards either as extracted oil or as dried kernel (" copra "). It is well known that the unripe coconut contains an endosperm floating in a milky, sacchariferous fluid which, as ripening proceeds, becomes converted into a fibrous deposit on the inner side of the shell. This deposit contains about 40 per cent. of coconut oil and, in the sun-and-air-dried state, is termed copra (fat content 63–65 per cent.).

Obviously the conditions under which the copra is dried determine the quality of the resulting oil, whilst the highest quality oil is obtained by extraction as soon as possible after gathering. This is now carried on to a considerable extent at or near the plantations where the coconut palm is cultivated, and the resulting crude coconut oil is of very high quality, pale, and containing only small percentages of free fatty acid.

This oil is naturally in greatest demand for edible fats, whilst oils extracted in Europe from copra are in general more suitable as soap material. Extraction is now almost universally carried out by hot-pressing ; formerly the copra was boiled with water and the supernatant fat skimmed off. The oil-cake from the extraction presses contains about 8 per cent. of fat and about 20 per cent. of proteins, and is in good demand as a cattle food.

Coconut oil and palm kernel oil (see below) are fats in which lauric acid occurs abundantly (40-50 per cent.), and the pre-eminence of sodium laurate amongst the soaps of the saturated fatty acids as regards detergent power, combined with free solubility and hardness, accounts for the value attached to these oils.

Palm Kernel Oil.—The West African oil palm, *Elaeis guineensis*, is the source of two widely used vegetable fats, palm kernel oil and palm oil. The fruit consists of a fleshy outer coat enclosing a hard seed about one inch in diameter, and consisting of a kernel enclosed in a very hard shell. The seeds are shelled on the palm plantations and the kernels are mainly exported and extracted in Europe or America ; the oil-cake left after pressing (or solvent extraction) is a serviceable food for cattle, and thus practically the entire kernel is of economic value in the countries where the fat is extracted. The seeds contain by weight about three parts of shell to one of kernel, the latter containing about 45 per cent. of extractable oil. Providing that the exported kernels have been maintained under reasonably dry and cool conditions prior to fat extraction, the resulting crude fat is almost white in colour and contains less than 5 per cent. free fatty acids ; large quantities of this quality of palm kernel oil are produced and used in the edible fat industry. Nuts of inferior quality yield somewhat dull-coloured fats which contain more free fatty acid and possess a characteristic musty odour ; the fat from these nuts, however, together with the mixed soap and oil resulting from treatment of the better oils for edible purposes, provides soap-making material of excellent quality.

Palm Oil.—It is convenient to deal here with the fat obtained from the remainder of the palm fruit, namely, the fleshy pericarp or fruit-coat which encloses the nut in much the same way as a plum fruit encloses the stone and kernel. This fruit-coat fat has, for obvious reasons, to be extracted more or less on the spot. It differs very markedly from the kernel fat in its composition and properties : whilst the kernel fat is relatively brittle, the pericarp oil is of the consistency of a butter fat or soft tallow, and somewhat resembles the latter in its composition (palmitic, oleic, and some stearic acid, very little myristic acid, and no acids of lower molecular weight).

Years ago, the fat was extracted by the natives, the crudest process consisting in allowing the fruits to decay in a heap until the oil separated and collected at the top of the mass (palm oil is liquid at tropical temperatures). Naturally such oil was highly rancid, and would contain 30 per cent. or more of free fatty acid ; furthermore, the unsaturated acid present was broken up to some extent, with the result that the fat was relatively of high melting-point. The cruder grades of present-day palm oil, which contain most free fatty acid and are of a harder texture and dull yellow-brown in colour, are termed Congo palm oil, or "hards," the name having originally been given to the inferior types of native-produced palm oil. Better qualities of the native-produced oil, "softs," containing 8-12 per cent. free fatty acid, are known as Lagos, Bonny, Benin, etc., palm oils and are softer fats of a clearer, bright reddish tint.

Under modern conditions the fruit is pulped, sterilized, and expressed by machinery installed at centres as near as possible to the palm plantations. Whereas formerly the fruit was collected from wild palms, much of the present production emanates from cultivated plantations, notably in the British West African Colonies, Nigeria, and the Belgian Congo, but also in Sumatra and Malaya ; owing, however, to the ease with which the fruits are bruised in collecting and transport to the extraction stations it is difficult completely

to eliminate hydrolytic decomposition, and best plantation palm oils, although bright red in colour and sweet-smelling, usually contain 3-5 per cent. of free fatty acid as received in Europe.

The oil is used extensively both for edible fat and for soap, its characteristic colour, due to minute proportions of carotin and xanthophyll, being usually removed by bleaching processes of various types (*cf.* Section III., Chapter II.) ; it is also used in the tin-plate industry as a protective coating against atmospheric oxidation of the hot metal.

Cohunc oil and Babassu fat are nut oils obtained from the seeds of various trees of the palm family which are abundant in some of the Central and South American forests. They are very similar in character to palm kernel oil and could generally be substituted for it ; the trees grow in the wild state in enormous quantities, and organization of transport facilities is all that is necessary to render these fats available on a large scale. Babassu fat, which has a slightly higher melting point than palm kernel oil, is commencing to supplement the use of the latter.

Murumuru fat, from the nuts of the Brazilian *Astrocaryum Murumuru*, is another fat producible in abundance and more or less similar to Babassu fat ; and there are a number of similar and potentially usable kernel fats from other members of the tropical palm family.

Cacao butter, the fat of the cocoa bean, is a yellowish-coloured fat which, although it melts below 35°, is particularly hard and brittle ; this property, which is due to its specific structure as a relatively simple mixture consisting mainly of oleopalmitostearin and oleodistearin, makes it especially suitable as a basis for confectionery. The fat is extracted from the dried beans in the processes of making cocoa powder and chocolate, and the extraction is therefore carried on as a rule at the chocolate factories. The shells of the cocoa beans contain a certain amount of fat which is sometimes extracted, but the value of the "cocoa-shell butter" for edible purposes is of a very low order. On the

other hand, the shells are unusually rich, after exposure to tropical sunlight, in vitamin D.

Chinese vegetable tallow, a wax-like incrustation which surrounds the seeds of *Stillingia sebifera*, a tree common in China and grown to some extent in India, finds some employment, in the best qualities, as a cacao butter substitute. Most of this fat is, however, used in China for candles and soap, and the quantities exported to Europe are at present not very large, and vary widely in quality, frequently containing excessive amounts of unsaponifiable matter and free fatty acid. (The seed fat itself, stillingia oil, is a liquid drying oil containing mainly linoleic and oleic glycerides, cf. Table IV., p. 128.)

Borneo tallow is used as a substitute for cacao butter; in the crude state it is a greenish fat obtained by pressure extraction of the nuts of various species of *Shorea*, which grow in Borneo and other islands of the Malayan Archipelago. The refined fat, apart from its colour (faint green instead of pale yellow), is almost identical in physical properties with cacao butter, but somewhat harder owing to the presence of more oleodistearin.

Nutmeg butter, although only used in relatively small quantities as a salve, is of interest as a representative of the fats from the genus *Myristica*, most of which are characterized by the presence of considerable proportions of trimyristin.

Japan wax, which is practically exclusively employed in polishes, is similarly interesting in that it consists very largely of tripalmitin; it occurs, like palm oil, in the outer coat of the fruit, the berries of *Rhus* (sumach) species containing the "wax" between the outer skin and the kernel.

Mowrah butter (also termed *mowrah seed oil* or *Illipé butter*) is the fat from the seeds of various species of *Madhuca* (*Bassia*) *latifolia*, a tree which is cultivated to a considerable extent in India and the East Indies. It could yield a very large output of fat per annum. The fat is of a buttery consistency and can be used for edible purposes, as a salve, and for soaps and candles; considerable quantities are

extracted in India for these ends. The mowrah oil-cake is poisonous and only available for manurial purposes.

Shea butter is very similar to mowrah fat and is derived from a West African tree *Butyrospermum Parkii*, which grows in abundance in the wild state in the Sudan and other parts of West Central Africa. It is used to some extent in Europe as a component of edible fats and in soaps, for both of which it is well suited, apart from its liability to contain small proportions of a hydrocarbon similar in properties to gutta-percha amongst its unsaponifiable contents. This hydrocarbon also accompanies the seed fats of several other members of the tropical family Sapotaceae, to which both mowrah and shea belong.

Another potentially useful seed fat, rich in oleodistearin, is that found in the kernels of different species of *Allanblackia*, shrubs which are abundant in North-West Africa. The fat of *A. Stuhlmannii* (Mkanyi tallow or butter) contains nearly 70 per cent. of oleodistearin, most of the remainder being stearodiolein.

Other tropical seed fats rich in stearic acid include those of *Garcinia* (Kokum, Gurgi nuts), *Pentadesma* (Kanya butter), *Vateria* (Dhupa or Malabar tallow), *Mimusops* (Dumori, Njave, Baku butters) and *Palaquium* (Njatuo tallow) species, belonging to the families Guttiferae or Sapotaceae. All these fats, with mowrah and shea butters, are especially good examples of the existence of potential fat resources which only require organized methods of collection and transport, together with the application of modern extraction processes.

II. Liquid Fats. The "Non-drying" Vegetable Oils.

The remainder of the vegetable fats can be best dealt with by arranging them, following Lewkowitsch, according to their capacity for absorbing atmospheric oxygen with the production of a solid transparent resin or lacquer due to the formation of "linoxyn." This property, which is roughly proportionate to the iodine absorption capacity of the oil, is most marked in the "drying oils" with per-

II. Liquid Fats.—The “Non-drying” Vegetable Oils.

(i) Occurrence.

Fat.	Source.	Habitat.	Approximate annual		Technical applications.	Fat-content.
			Production.	Imports to U.K.		
OLIVE OIL; Olive kernel oil.	Olea europaea ssp. <i>tiva</i> .	Mediterranean sea-board, Syria, Algeria, S. Africa, and Australia.	Tons. 800,000- 1,000,000	Tons. 10,000- 12,000	Salad and other edible oils; lubricant, pharmacy, soap.	30-60% (fruit); 25-28% (kernels).
GROUNDNUT OIL (Earthnut, peanut, arachis).	Arachis hypogaea	West Africa, E. Indies, China, U.S.A., South America, etc.	750,000- 1,000,000	75,000- 120,000	Edible fats and soap.	40-50% (kernels) 32-36% (undecorticated).
Almond oil ..	Prunus amygdalus	Southern Europe, N. Africa, Asia Minor.	—	—	Edible oil, pharmacy.	40-55% (kernels).
Apricot kernel oil	P. <i>armeniaca</i> ..	France, etc. ..	—	—	Almond oil substitutes.	40-45% (kernels).
Peach kernel oil	P. <i>persica</i> ..	Temperate and subtropical Europe.	—	—		32-35% (kernels).
Plum kernel oil ..	P. <i>domestica</i> ..	Temperate climates ..	—	—		40-42% (kernels).
P. <i>damascena</i> ..			—	—		10-15% (meal).
Rice oil ..	Oryza sativa ..	Burmah, Japan, U.S.A., Italy.	—	—	Pharmacy; lubrication, “Turkey-red” oils.	45-50% (seeds).
CASTOR OIL ..	Ricinus communis	East Indies, U.S.A., Mediterranean.	70,000	15,000		
RAPE OIL (Colza)	Brassica campestris v. B. <i>campestris var.</i>	Europe, India, Malaya, Russia, Danube, Black Sea. N.W. India	150,000- 250,000	20,000	Edible oils, salads, lubricants, burning.	35-45% (seeds).
RAVISON OIL ..	B. <i>campestris var.</i>	N.W. India		—	Burning, lubricant.	33-40% (seeds).
JAMBA RAPE OIL	Brassica <i>sp.</i> ..	N.W. India		—	Burning, inferior to colza oil.	26-33% (seeds).
Black mustard seed oil.	Brassica (<i>Sinapis</i>) <i>nigra</i> .	India, E. Africa ..	—	—	—	31-33% (seeds).
White mustard seed oil.	B. (<i>S.</i>) <i>alba</i> ..	Europe, India	—	—	—	25-36% (seeds).

(ii) Average Analytical Characteristics.

Fat.	Sp. gr. 15°/15°.	Ref. index.	Setting pt.	Sap. Val.	Sap. Eq.	Iodine absn. %	Acetyl Value.	Combined fatty acids.		Free fatty acids.		% Unsap.
								Titer.	M. pt.	Acid Val.	Aspartic acid.	
Olive Oil ..	0.914-0.920	1.471/15°	Below 0°	189-195	287-298	80-85	5-11	17-21°	22-28°	2-20	1-10% 10-70%	0.5-1.5% 2-3%
SULPHUR ..	"	"	"	"	"	"	"	"	"	—	—	—
Olive Oil ..	0.918-0.920	1.468/25°	—	181-189	298-309	82-87	—	—	—	—	Trace	Traces
Olive kernel oil ..	—	—	—	—	—	—	—	—	—	—	—	—
GROUNDNUT Oil (Arachis, peanut, earthnut) ..	0.916-0.921	1.473/15°	0-3°	189-196	286-298	85-98	3-9	23-29°	27-35°	2-6	1-3% 1-18	0.3-1.0% 0.5-9%
Almond oil ..	0.914-0.920	1.473/15°	-10 to -20°	188-192	292-298	93-100	—	9-10°	13-14°	—	—	—
Apricot kernel oil ..	0.915-0.921	1.471/20°	-14 to -20°	188-198	283-298	96-112	—	0-6°	12-15°	1-12	0.5-6% 1-12	1.2%
Peach kernel oil ..	0.918-0.923	1.472/20°	-20 to -23°	189-196	286-297	92-110	—	5-13°	12-19°	1-12	0.5-6% 1-12	—
Plum kernel oil ..	0.916-0.921	1.471/20°	-5 to -17°	188-198	283-298	91-104	—	12-15°	20-22°	—	—	0.6%
Rice oil ..	0.913-0.928	1.470/25°	-5 to -10°	183-192	292-306	100-108	—	28-29°	31-36°	up to 12	up to 6% 0.15-0.70	3-5% 0.3-0.6%
CASTOR Oil ..	0.950-0.974	1.480/15°	-10 to -18°	176-187	300-318	81-89	146-154	3°	13°	0.3-4	—	—
RAPE OIL (Colza) ..	0.911-0.918	1.475/20°	-4 to -10°	172-175	320-326	94-106	1-6	12-18°	16-21°	0.6-12	0.3-6.0% 1.5-2.0%	0.5-1.5% 1.5-2.0%
(RAVISON OIL JAMBA RAPE) Oil ..	0.915-0.922	1.475/20°	-8 to -10°	173-181	309-324	105-120	—	—	—	—	—	—
Black mustard seed oil ..	0.913-0.918	1.472/20°	-8 to -12°	169-175	320-331	95-102	—	8-16°	12-21°	—	—	0.5-1.0%
White mustard seed oil ..	0.914-0.923	1.467/15°	-11 to -17.5°	173-176	318-325	96-107	—	6-17°	9-18°	1-7	0.5-3.5% 1.0%	1%
..	0.912-0.916	1.475/15.5°	-8 to -16°	170-178	315-330	93-109	—	9-10°	12-16°	1-7	—	1%

centage iodine absorption of 130–180, less so in the “semi-drying oils” with iodine values of 100–140, and absent in the “non-drying oils” with iodine absorption below about 100–110 per cent.

Since rancidity is closely connected with oxidation effects, it is natural that the “*non-drying oils*” comprise nearly all the liquid fats which can be utilized as such (*i.e.* without partial saturation by hydrogenation) for edible purposes. These fats are also valuable as soap-making materials, as lubricants, in some cases as illuminants, and also in pharmacy, both for internal administration and in ointments.

With the exception of the rape oil group, the members which it is desirable to notice here do not possess genetic connections of the kind subsisting between the members of some of the various sub-groups of the vegetable butter group.

Olive oil is the typical example of a “non-drying oil.” The cultivation of the olive, formerly confined to the coastal districts of the Mediterranean, is now practised in California and also in Australia and South Africa. The olive fruit consists of about 95 per cent. of fleshy pericarp containing from 30 to 60 per cent. of oil, and about 2·5 per cent. of kernel containing 25–30 per cent. of oil; the kernel oil, in contrast to that of, for example, the oil palm or *Stillingia*, is of almost exactly the same chemical composition as the fruit-coat oil.

The finest edible qualities of olive oil are produced by cold-pressing the fruits (in the absence of the kernels); more ordinary grades of edible oil are produced by hot-pressing of the cold-pressed pulp (with or without the kernels), whilst, finally, low grades of oil, usually termed *sulphur olive oil*, are obtained by extraction of the hot-pressed residues with solvents, usually carbon disulphide.

The intermediate grades of oil are used in the manufacture of high-grade toilet and other soaps, and as textile oils, whilst the lowest grades of sulphur olive oil, which are usually high in free acidity and deep green in colour, are also employed for the cheaper brands of toilet soap and Castile

soap. They would provide excellent high-class soap-making materials if the deep colour could be effectively removed.

Owing to the high price usually commanded by olive oil, a number of substitutes for it have come into the market, especially for use in the textile industries. These include slightly hydrogenated groundnut oil, re-processed olive oils made by esterification of crude olive oil (distilled) acids, or of olive oils of high free acidity, with glycerine, and also olive oil or similar mixed fatty acids combined with other alcohols (*e.g.*, cyclohexanol) in place of or as well as glycerine.

The intensive extraction of oil which is practised renders the residual cake of little or no feeding value, although it finds some application as a manure.

Groundnut oil (arachis, peanut, earthnut oil).—The source of this fat is the groundnut or peanut, a tropical or semi-tropical fruit which is familiar in consequence of the extent to which it is imported for consumption in the natural state. It consists of a pale-coloured fragile husk enclosing a loose elongated kernel which is coated with a thin reddish skin. The nuts are imported, mainly from West Africa, either in the husks (undecorticated) or as the red-coloured kernels (decorticated). The undecorticated nuts keep better and are preferred for the best qualities of edible groundnut oil; the kernels contain about 40–50 per cent. expressible fat.

Extraction is effected by cold- and hot-pressing; the nuts are decorticated by machinery, and subsequently the reddish skin is similarly removed (this may be added to the cold-pressed cake prior to hot-pressing, as it contains appreciable quantities of fat).

The cold-pressed oil provides, on refining, a useful salad and edible oil, whilst the oils recovered at a higher temperature find application in soap-making and to some extent as an illuminant. The residual cake contains about 8 per cent. of oil and considerable protein (5–8 per cent. of nitrogen and 1–1·5 per cent. of phosphoric acid), and in consequence of the latter is exceptionally valued for cattle-feeding purposes.

Almond oil is generally prepared from bitter almonds, which contain about 40 per cent. of oil. The oil is expressed in much the same way as groundnut oil, but is of very high edible value and is also used considerably in pharmacy ; in consequence it is high in price and therefore invites adulteration. The kernel oils of the apricot, peach, and plum are most frequently substituted for or added to genuine almond oil ; as they are almost identical therewith in the usual characteristics, specific "colour" tests of an empirical character must be relied upon for discriminating between these four oils.

Rice oil can be prepared from rice meal, which contains about 10-15 per cent. of oil ; it is mentioned here because, although hitherto little exploited as a soap-making material, it is a possible source of supply where economic conditions would permit.

Castor oil is an important "non-drying oil" with special properties as a purgative, as a lubricant for petrol-driven motors, and as a source of certain sulphonated derivatives employed in alizarin dyeing ; it stands apart from the rest of this group by reason of its composition, consisting very largely of the triglyceride of ricinoleic acid, 10-hydroxyoleic acid. As a result of the presence of the hydroxyl group, the viscosity of castor oil is much greater than that of the ordinary fatty oils.

The oil is obtained from the seeds of the castor oil plant, *Ricinus communis*, by cold expression (for medicinal qualities) and by hot expression or solvent extraction (for oils of somewhat less high quality).

The Rape Oil Group.—This sub-group is on the border line between "non-drying" and "semi-drying" oils and comprises various commercial oils obtained from different species of the *Brassica* family ; they all contain notable proportions of the glyceride of erucic acid, $C_{22}H_{42}O_2$, and are employed as edible oils, illuminants and lubricants.

The most important is *rape* or *colza oil*, which is obtained from the seeds of the rape plant, *Brassica campestris*, which is cultivated in several varieties in South-Eastern Europe

III. Liquid Fats.—The “Semi-drying” Vegetable Oils.

(i) *Occurrence.*

Fat.	Source.	Habitat.	Approximate annual		Technical applications.	Fat-content of seeds.
			Production.	Imports to U.K.		
COTTONSEED OIL	Gossypium hirsutum " barbadense " herbaceum, etc.	U.S.A. .. Egypt and Sudan India, Asia Minor .. Tropical zones of Asia, Africa, and America.	.. over 1,100,000 .. —	100,000- 120,000 ..	Tons. Margarine and other edible fats; soap- making; steel- plate industry. Cottonseed oil substitute in soap-making and edible fats. Edible fats, lu- bricants, soap.	35-40% (kernels). 20-25% (whole seed). 35-40% (kernels). 50-55% (seeds). 50% (germs).
KAPOK OIL	Bombax and Eriodendron species.	2,000	—	—
SESAME OIL	Sesamum indicum	East Indies, Eastern Asia, Asia Minor, East and West Africa. U.S.A., Argentine ..	100,000- 150,000 ..	—	Edible fats and soap.	12-17% (germs).
MAIZE OIL	Zea mays	..	50,000- 100,000 ..	—	—	—
WHEAT OIL	Triticum vulgare.	Temperate zones	—	Mainly in soap- making; also edible fats.	22-32% (whole seed).
SUNFLOWER-SEED OIL	Helianthus annuus	Eastern Europe, China, S. Africa.	over 100,000	small	—	—
CROTON OIL	Croton tiglium ..	S. India and China ..	—	—	Pharmacy.	55%

(ii) Average Analytical Characteristics.

Fat.	Sp. gr. 15°/15°.	Ref. index.	Setting pt.	Sap. Val.	Sap. Eq.	Iodine abn. %	Acetyl Value.	Combined fatty acids.		Free fatty acids.		% Unsap.
								Titer.	M. pt.	Acid Val.	As oleic acid.	
COTTONSEED Oil . .	0.913-0.930	1.474/15°		191-196	286-294	103-111	—	33-38°	34-40°	2-6	1-3%	0.7-1.6%
KAPOK Oil . .	0.923-0.926	1.466/40°		189-196	286-297	86-98	—	27-32°	32-36°	2-20	1-10%	0.7-1.1%
SESAME Oil . .	0.921-0.924	1.475/15°	-4° to -6°	188-195	288-298	103-112	—	21-24°	23-32°	1-10	0.5-5%	1-1.5%
MAIZE Oil . .	0.920-0.928	1.477/15.5°	-10° to -15°	188-193	291-298	117-130	—	15-19°	17-22°	2-20	1-10%	1.5-2.5%
Wheat oil . .	0.924-0.929	1.483/20°	0°	183-190	295-307	115-120	—	29-30°	39-40°	about 10	5%	2-5%
SUNFLOWER SEED Oil . .	0.920-0.926	1.473/25°	-16° to -18°	186-194	290-300	127-136	—	17-20°	21-24°	6-12	3-6%	0.3-0.5%
CROTON Oil . .	0.938-0.943	1.478/26°	-8° to -18°	200-215	260-280	102-109	20-40	18-19°	17-19°	—	—	0.2-0.6%

and in Eastern India and Malaya. The seeds, which are similar in appearance to turnip or mustard seed, are crushed and either pressed or solvent-extracted, the yield of oil being about 40 per cent. of the seed. The residual pressed cake is a useful cattle food.

The oil comes on the market in several qualities, e.g. *colza oil* for salad and edible oil and for lamps, and *rape oil* of somewhat lower quality used as illuminant and lubricant; whilst *ravison oil* or *Danubian rape oil* is held in general as slightly inferior to rape oil, and finally *Jamba rape oil*, from an East Indian source, is liable to contain organic sulphur compounds and is usually classified as a low-grade rape oil.

The *mustard-seed oils* closely resemble rape oil in all characteristics, but are more expensive and are thus of no great technical interest.

III. Liquid Fats.—
The “Semi-Drying” Vegetable Oils.—This group comprises certain oils which, although in some degree by-products of other industries, are used on a

very large scale both in edible fats and in soaps. For the former purpose they supply the more liquid fatty constituents to materials of the margarine type in place of lard or tallow oils, but, in view of their content of linoleic glycerides, care must be exercised in the proportion employed in order to escape tendency to development of rancidity on storage. Similarly, their value in soaps is due to the abundance of oleic and linoleic acids which, present in considerable proportions, conduce to the production of free lather and good detergent power; at the same time, in contrast to the soaps from "drying" oils, in which linoleic acid preponderates and is often accompanied by some proportion of linolenic acid, the soaps from the present group of oils do not undergo atmospheric oxidation to any marked extent on keeping.

Cottonseed oil is the most prominent member of the group, since it is always available in the seed left after removal of the fibre for textile manufacture. It is produced on a very large scale in the United States by expression of the crushed, decorticated seeds, which contain about 40 per cent. of oil; further large amounts are prepared in Europe by expression mainly of Egyptian and Indian as well as of American seed. The seed-cake is used as a feeding-stuff for cattle. Owing to the presence of colouring matter (flavone derivatives) in the seed the crude oil is deep yellow or reddish coloured, but the coloured compounds are largely removed by treatment with a little caustic soda; the mixture of cottonseed oil soap and emulsified oil which settles out is sold as "C.S.O. soap-stock" and employed in soap-making.

Kapok oil is obtained from a number of tropical trees the seeds of which are very similar to those of the cotton plant, but are smooth and not hairy. The oil is very similar in composition to cottonseed oil, and could be used at will for the same ends as the latter to a much greater extent than is at present the case.

Sesame oil or *teel oil* is a compulsory constituent of butter substitutes in several Continental countries, in order

to afford an easy means of distinction of the product by means of the Baudouin colour test, which is a reliable indication of the presence of this oil (*cf.* Section I., Chapter IV.). The seed, which contains about 50 per cent. of oil, is imported from India, China, and West Africa and treated mainly at Marseilles, Hamburg, or in Holland by expression or extraction. Although good quality edible oil is readily producible, sesame oil has not yet been utilized very largely in Britain either for this purpose or for soap ; but there seems to be no reason why it should not be employed. The expressed cake is an excellent cattle food, and the solvent-extracted cake, although too deficient in oil for feeding purposes, is valued on the Continent as an artificial fertilizer.

Maize (corn) oil is produced on a considerable scale in the United States by expression of the germs of the maize or Indian corn seed : the starchy matter in the latter is the raw material for large quantities of glucose, when the starch is first of all separated from the germ either by winnowing or in the moist state after malting. The germs are then pressed in order to obtain the 40–50 per cent. of oil present, which is thus a by-product of the glucose industry, just as cottonseed oil is a by-product of the cotton trade. It has a broad chemical similarity to cottonseed oil, but absorbs oxygen distinctly more readily and thus has greater tendency to rancidity and no utility as a lubricant. The oil is used in some varieties of edible fat, although it is difficult to free it from a distinctive grain-like flavour ; it is also used in soap-making in America, but is not at present employed to any great extent in Britain. The oil-cake is not so highly valued as cottonseed cake.

Wheat oil is very similar in characteristics to maize oil, but was of no great technical interest until recent years, probably because the wheat germ contains only about 15 per cent. of oil. It has now become of greater importance owing to the fact that it contains considerably higher concentrations of vitamin E (tocopherol) than most fatty oils.

Sunflower seed oil is often classed as a "drying" oil, but

its properties are probably more nearly allied to those of maize oil than to those of the more definitely "drying" oils. At the same time, it does not possess the full yellow colour and the grainy taste of maize oil, and can in fact be refined to a colourless, odourless, and almost tasteless condition. It is therefore rather curious that the oil is not more extensively produced, and, in fact, from seed grown in Britain, the soil and climate being eminently suitable. The seeds contain about 30 per cent. of expressible oil, leaving an oil-cake containing about 8-10 per cent. of oil which, again, is not used as it might be in Britain, although in Scandinavian countries it is priced between linseed and cottonseed cake in virtue of its value as a dairy-cattle food. There appears to be a case for consideration whether home-grown sunflower seed oil and cake ought not to take the place of at all events some of the American products of a similar type, with resulting benefits to agriculture as well as the fat and soap industries.

Croton Oil bears the same relation to this group of oils as that of castor oil to the "non-drying" oils, namely, it is a very viscous oil of strong purgative properties, is optically active, and possesses a definite acetyl value (which, however, is much lower than that of castor oil). Its chemical composition is not well known in detail, but it is quite unlike castor oil in that it contains little or no ricinolein. It is employed practically exclusively in pharmacy.

IV. Liquid Fats. The "Drying" Vegetable Oils.

As the iodine absorption or, rather, the mean unsaturation, of the fats increases we pass from those which are mainly useful for soaps to others which, whilst frequently components of soft soap, are chiefly employed in the paint and varnish industries as vehicles which on exposure in a thin layer to air set to a hard vitreous film, owing to absorption of atmospheric oxygen.

Naturally the transition is not abrupt, and thus, whilst some of the oils of high iodine number in the "semi-drying" group show definite "drying" capacity, it will be seen that

IV. Liquid Fats.—The "Drying" Vegetable Oils.

(i) Occurrence.

Fat.	Source.	Habitat.	Approximate annual production		Technical applications.	Fat-content of seeds.
			Tons. Production.	Tons. Imports to U.K.		
SOYA BEAN Oil	<i>Soja japonica</i> , syn. <i>hispida</i> .	Manchuria, China, Japan, East Indies, S. Africa, U.S.A.	Tons. 250,000- 300,000	Tons. 25,000- 50,000	Soap-making ; linseed oil substitute.	15-20% (seeds).
Safflower oil ..	<i>Carthamus tinctorius</i>	Caucasus, India, E. Africa W. Indies, Mexico, India	could be abundant, could be abundant.	—	Soap and linseed oil substitute.	25-32% (kernels).
Argemone oil ..	<i>Argemone mexicana</i>	Western Europe, N. Africa, N. America, India, and Japan.	15,000- 25,000	—	Lamp oil, lubricant, paints.	34-38% (kernels).
Hempseed oil ..	<i>Cannabis sativa</i> ..	France and Germany ..	—	—	Paints and varnishes, soft soap.	30-35% (kernels).
" ..	<i>Juglans regia</i> ..	Egypt, Asia Minor, Persia, India, China.	12,000	—	Artists' paints and var- nishes ; edible and illuminants ; soft soap.	63-65% (kernels).
Poppy seed oil ..	<i>Papaver somniferum</i>	E. India, Malaya, S. America, Pacific Islands, W. Indies, Brazil.	25,000	—	Artists' paints and var- nishes ; illuminants ; soft soap.	45-50% (kernels).
Rubberseed oil ..	<i>Hevea brasiliensis</i> ..	China, also India	—	—	Good drying oil for paints.	50% (kernels).
Candlenut (Lum- bang) oil ..	<i>Aleurites moluccana</i>	—	—	—	Illuminant ; linseed oil substitute as drying oil or in soft soaps.	55-65% (kernels).
Stillingia oil ..	<i>Stillingia sebifera</i> ..	—	—	—	Good drying oil ; lamp oil.	40-50% (kernels).
Perilla oil ..	<i>Perilla ocimoides</i> ..	Japan	5,000- 10,000 (?)	Good drying oil.	35-45% (kernels).
Oiticica oil ..	<i>Licania rigida</i> ..	Brazil	—	Good drying oil for varnishes.	50-60% (kernels).
CHINA Wood Oil ..	Aleurites Fordii, mon- tana.	China and Japan ..	100,000	—	Excellent drying oil for varnishes.	40-50% (kernels).
LINSEED Oil ..	<i>Linum usitatissimum</i>	Russia, Hungary, France, Ireland, U.S.A., and Canada, Argentine, N. India.	1,000,000- 1,500,000	100,000- 150,000	Excellent drying oil ; paint and varnish in- dustry ; soft soap.	35-40% (kernels).

(ii) *Average Analytical Characteristics.*

Fat.	Sp. gr. $13^{\circ}/15^{\circ}$	Ref. index.	Setting pt.	Sap. Val.	Sap. Eq.	Iodine absn. % /0	Combined fatty acids.		Free fatty acids.		% Unsap.
							Titer.	M. pt.	Acid Val.	As oleic acid.	
Soya Bean Oil	0·924-0·927	1·468/40°	-8° to -18°	190-193	291-296	124-133	21-24°	26-29°	2-7	1-3-5%	0·2-0·6%
Safflower oil ..	0·923-0·928	1·477/16°	-13° to -20°	187-194	289-300	130-150	11-16°	16-18°	2-10	1-5%	0·7-1·5%
Argemone oil ..	0·925-0·926	1·466/40°	—	187-190	296-300	119-122	22°	22°	—	—	1-0%
Hempseed oil ..	0·925-0·933	1·475/15°	-15° to -25°	190-195	287-296	145-165	15-17°	17-21°	—	—	1·0-1·3%
Walnut oil ..	0·924-0·927	1·480/15°	-15° to -28°	190-197	284-296	140-150	13-16°	15-20°	—	—	0·2-0·4%
Poppy seed oil ..	0·924-0·927	1·478/15°	-15° to -20°	189-196	286-297	132-143	15-17°	20-21°	1-10	0·5-5%	0·5-0·7%
Rubberseed oil	0·923-0·932	1·473/25°	—	186-196	286-301	127-144	27-33°	—	Ca. 10	Ca. 5%	0·7-1%
Candlelent oil ..	0·920-0·927	1·479/20°	-15° to -20°	189-195	287-297	155-165	13-15°	18-21°	2-8	1-4%	Ca. 1%
Stillingia oil ..	0·939-0·946	1·482/25°	—	203-210	267-276	146-170	12°	15°	10-16	5-8%	0·4-1·5%
Perilla oil ..	0·930-0·937	1·483/20°	—	187-197	284-300	180-206	—	-4 to -5°	1-8	0·5-4%	0·4-1·5%
Oiticica oil ..	0·968	1·504/40°	—	186-194	289-301	139-155*	—	—	2-6	1-3%	0·5-1·0%
CHINA WOOD OIL	0·936-0·949	1·523/15°	2-3°	189-195	287-297	160-180*	31-37°	35-44°	0-12	0-6%	0·4-1·0%
Linseed Oil ..	0·932-0·938	1·484/15°	-18° to -27°	189-196	286-297	170-185	19-21°	20-24°	1-8	0·5-4%	0·5-1·5%.

* Indefinite, owing to conjugated unsaturation.

the present group comprises similar variations in relative unsaturation. We may take soya bean oil and linseed oil as respectively typical of moderate and strongly "drying" oils.

Soya Bean Oil has come into prominence during the present century and is now imported, either as seed or oil, in large quantities from Manchuria, and its cultivation is being undertaken in many parts, especially in the United States (the plant accommodates itself to either temperate or sub-tropical climates). The beans, which are pale globular seeds somewhat resembling a large cream-coloured sweet pea seed, contain up to 20 per cent. of oil which is extracted by expression or by solvent; their protein and sacchariferous content is high even for a leguminous plant, and consequently the residual oil-cake is a very rich cattle food and in good demand. The oil can be substituted to some extent for cottonseed oil in soap-making, and after partial hydrogenation may be utilized either for edible fat or as a tallow substitute in soap and candles. The "drying" properties of the original oil are also utilized, especially in the production of linoleum.

Safflower oil, from the saffron, *Carthamus tinctorius*, which can be grown in quantity in many Asiatic countries; *argemone oil*, from the prickly poppy, which occurs wild in unlimited quantities in Central America and India; and *hempseed oil*, also procurable in large quantity from the hemp plant, *Cannabis sativa*, are sufficiently close in composition to soya bean oil to make it probable that they could be substituted for it if desired.

Linseed oil is the most widely used and typical "drying" oil for paints, varnishes, linoleum manufacture, etc. It is mainly extracted from the flax seed by pressing, since this process yields both a better "drying" oil and a residual cake of high feeding value; the solvent extraction process is also, however, used to some extent. The "raw" oil is in many cases "boiled" in order to clarify it and improve its "drying" properties: this implies heating the oil to about 250° C. in a closed vessel, when a certain proportion

of suspended particles of mucilage, etc., are coagulated and also, doubtless, some polymerization of the linoleic and linolenic glycerides present commences to take place.

Linseed oil is also largely used in manufacturing soft soap.

It should be noted that the main constituents (about 80 per cent.) of the fatty acids of linseed oil are linoleic and linolenic acids, in more or less similar proportions.

Walnut oil and *poppy seed oil* are produced in amounts which are small compared with linseed oil, but are important because they are very pale in colour, whereas linseed oil is always pale to deep yellow. In consequence of the absence of colour, these oils, which have practically the same "drying" properties as linseed oil, are used in the production of the most superior classes of paints and notably in artists' colours.

Rubberseed oil, from the seeds of *Hevea brasiliensis*, is a good drying oil and could be produced as a by-product of the rubber plantation industry; the seeds (with shells) contain about 30 per cent. of oil which would probably repay collection and extraction by modern plant.

Candlenut (lumbang) oil and *Stillingia oil* are two instances of oils present in the seeds of trees which, having good "drying" properties, might be serviceable as substitutes to some extent for linseed oil.

Perilla oil, a Japanese product, is not produced on a very large scale, but is of interest in that it possesses an iodine absorption of an even higher order than linseed oil and in consequence "dries" still more rapidly.

China wood or *tung oil* is the next most important drying oil after linseed oil. It is produced from the seeds of two small trees or shrubs, *Aleurites Fordii* and *A. montana*, indigenous to China; the Japanese *A. cordata* yields a similar oil, but other members of the *Aleurites* genus do not always contain in their seed fats the elæostearic acid which confers its specific properties on tung oil. The presence of the conjugated triethylenic elæostearic glycerides

V. Solid Fats.—Chaulmoogra oil Group.

(i) Occurrence.

Fat.	Source.	Habitat.	Technical applications.	Fat content of kernels.
Chaulmoogra oil ..	Taraktogenos Kurzii ..	Burmah and Assam ..	Used in pharmacy.	48–55%
Hydnocarpus oil ..	Hydnocarpus Wightiana ..	Western India ..	" "	60%
Lukrabo oil ..	Hydnocarpus anthelmintica ..	Siam and Indo-China ..	" "	60%

(ii) Average Analytical Characteristics.

Fat.	Sp. gr.	Ref. index.	Setting pt.	Optical activity [α] _D °	Sap. Val.	Sap. Eq.	Combined fatty acids.		Free fatty acids.		% Urt.-sap.
							Iodine absn. %	Titer.	M. pt.	As oleic acid.	
Chaulmoogra oil ..	0·951/25°	1·478/25°	5–20°	+51–56°	197–208	269–284	97–105	39–41°	44–47°	ca. 10	ca. 5%
Hydnocarpus oil ..	0·958/25°	1·478/29°	11–18°	+54–58°	197–208	269–284	93–103	40–42°	41–44°	ca. 4–8	ca. 2–4%
Lukrabo oil ..	0·953/25°	1·473/30°	20–25°	+47–54°	201–212 (m.p.)	264–279	83–91	36–41°	42–43°	ca. 8	ca. 4%
											1%

These oils are not obtained in very large quantities, but are interesting (i) because of their use in the treatment of skin diseases, including leprosy, and (ii) because they contain acids (chaulmoogric and hydnocarpic) which have been shown to contain a cyclic (5-membered ring) structure (*c.f.* Section I., Chapter II.). The oils are thus in some sense vegetable analogues of the naphthenic acids of petroleum (*c.f.* P. 182).

in this oil causes it to polymerize by the action of heat and oxidation more readily and to a more massive film than does linseed oil. Consequently tung oil is much in demand by varnish makers, and the Asiatic native supply is supplemented by tung oil from plantations of the trees cultivated in Florida and, to a certain extent, in some parts of the British Empire.

Oiticica oil, from the nuts of a Brazilian forest tree, has very similar properties to tung oil; its glycerides contain considerable amounts of keto-elæostearic acid, which causes them to have similar properties of polymerization to those of tung oil, although the presence of the ketonic group alters the characteristics of the polymerized varnish film in certain respects. *Oiticica oil*, whilst a possible supplement or substitute of tung oil, is not likely to displace the latter in the industry, owing to the differences mentioned in its varnish properties and to the circumstance that the parent tree takes many years to come to maturity and is thus unsuitable for cultivation as a source of the oil.

ANIMAL FATS

I. Solid Fats.—Butter Fats.—It is unnecessary to deal here at any length with the subject of ordinary *butter fat*, since its constitution is discussed in the next chapter and some further consideration is given to it in the chapter on Butter in Section IV. (Chapter I., p. 285). The characteristics in the accompanying table illustrate the fundamental distinction between butter fats and all other fats (save perhaps those from the coconut and palm kernel), namely, the presence of appreciable quantities of glycerides of fatty acids volatile in steam, the occurrence of combined butyric acid being unique.

A few data for butter fats from the European sheep, goat, and reindeer have been added in order better to illustrate the characteristic composition of milk fats in general, whilst the Indian *Ghee butter* (from the milk of the Indian cow, buffalo, or goat) is quoted on account of its widely extended use as an article of the native diet.

ANIMAL FATS.

I. Solid Fats.—Butter Fats.

(i) Occurrence.

Fat.	Source.	Habitat.	Approximate annual production.	Imports to U.K.	Technical applications.
			Tons. Probably over 1,500,000	Tons. 450,000- 500,000	Food.
BUTTER FAT ..	Cow's milk ..	Chiefly produced in Denmark, Ireland, Holland, France, Sweden, in Europe; Australia and New Zealand; Canada, U.S.A., etc.	—	—	—
Ghee butter ..	Cow, buffalo or goat milk.	India.	—	—	—
Goat butter ..	Goat's milk ..	Europe.	—	—	—
Sheep butter ..	Sheep's milk ..	"	—	—	—
Reindeer butter ..	Reindeer milk ..	N. Europe.	—	—	—

(ii) Average Analytical Characteristics.

Fat.	Sp. gr.	Ref. index.	Setting pt.	Melting pt.	Sap. Val.	Sap. Eq.	Iodine absn. %	Reichert-Messl. Value.	Combined fatty acids.		% Unsap.	
									Titer.	M. pt.	Acid Value.	
BUTTER FAT	0·936-0·944 15/15°	1·460/23°	19-24°	28-33°	216-235	237-260	26-45	21-36	33-38°	38-45°	0·4-2	0·2-1% 0·3-0·5%
Ghee butter	0·863 99/15°	1·453/40°	24-28°	31-38°	221-230	244-254	30-37	26-34	—	—	2-8	1-4% 0·4%
Goat butter	0·867 99/15°	1·456/40°	24-31°	27-38°	221-240	234-254	21-39	20-29	—	—	—	—
Sheep butter	0·869 99°/15°	1·455/40°	—	29-30°	216-240	234-260	25-38	23-33	—	—	—	0·5-3% —
Reindeer butter	0·864 99/15°	1·465/25°	34-39°	37-42°	219	256	23-25	31-35	—	—	—	—

II. Solid Fats.—Domestic Mammalian Body Fats.

(i) Occurrence.

Fat.	Source.	Main centres of production.	Approximate annual		Technical applications.
			Production.	Imports to U.K.	
LARD	Pigs ..	Mainly America; also Germany and Scandinavia.	Tons, Probably 750,000-1,000,000	Tons, 75,000-120,000	Food (margarine, confectionery); perfumes.
Skin grease ..	Ditto.	Ditto.	—	—	Soap; lubricant.
BEEF TALLOW ..	Oxen ..	Europe, Australia, N. and S. America.	Probably about 1,000,000	50,000-100,000	Margarine, soap, candles, etc.
MUTTON TALLOW ..	Sheep ..	Europe and America	—	Soap; candles.
Bone fat ..	Oxen and sheep ..	Europe and America ..	—	—	Lower grade soaps; candles.
Wool fat and wool grease.	Sheep's wool ..	As tallow	Very large	—	"Landolin."

II. Solid Fats.—Domestic Mammalian Body Fats.—The fats derived from the bodies of the pig, ox, and sheep are naturally of extraordinary importance to the oil and fat industries, although their production is so much more standardized, and also older than that of the vegetable fats and the marine animal and fish oils, that they are in some risk, as it were, of being taken for granted. Also, since both in Europe and America a considerable proportion of the fats of these animals is rendered and utilized for home consumption in a large number of installations, it is difficult to obtain reliable statistics which will illustrate with any accuracy the very large annual production of lard and tallow and the corresponding by-products, skin greases, bone fat, and wool fat.

The following notes will serve to indicate some of the characteristics of each product.

Lard.—The various qualities of lard are usually standardized in accordance with the custom of the

(ii) *Average Analytical Characteristics.*

Fat.	Sp. gr.	Ref. index.	Setting pt.	M. pt.	Sap. Val.	Sap. Eq.	Iodine absn. %	Combined fatty acids.	Free fatty acid.	% Unsap.	
										Titer.	M. pt.
LARD ..	0·934-0·938/15°	1·441/60°	22-32°	28-48°	193-200	280-290	46-66	34-42°	35-47°	0·5-1·3	0·2-0·7%
Skin grease ..										0·5-1·3	0·2-0·4%
BEEF TALLOW ..	0·937-0·953/15°	1·451/60°	30-38°	40-50°	190-200	280-295	32-47	38-47°	41-47°	1-50	0·5-25%
MUTTON TALLOW	0·937-0·961/15°	1·450/60°	32-45°	44-49°	192-198	283-291	31-47	39-52°	41-57°	1-50	0·5-25%
Bone fat ..	0·914-0·916/15·5°	—	15-17°	21-22°	184-195	287-304	43-56	36-42°	41-45°	30-60	0·5-2%
Wool fat and wool grease.	0·941-0·945/17°	1·480/40°	30-40°	31-42°	100-110	(510-560)	15-30	40°	41-42°	10-60	35-50% (alcohols)

Middle West of the United States of America, and are briefly as follows :

The highest qualities are obtained by vigorous agitation of the minced fat with warm water (below 50° C.) in specially dried agitators or rendering kettles, and are termed *neutral lard*; that from the kidney and neighbouring organs is known as No. 1 quality, that from the back as No. 2.

The cool-rendering process only removes a certain proportion of the fat, and the remainder of the material, either from the kidneys or back, is then rendered by treatment with water in autoclaves at above 100° C.; the product is termed *leaf lard* and is still of high edible quality.

A lower edible quality, *choice lard*, is obtained when the rendering at this stage has been carried out in open agitators heated by steam coils, whilst the lowest edible quality, *prime steam lard*, results from the autoclaving of other parts of the pigs than the kidney and back, with the exception of the other intestinal organs.

From the various qualities of lard thus produced, which vary in consistency and composition according to the part of the animal from which they emanate, liquid *lard oil* and tallowy *lard stearin* are prepared by chilling slightly and pressing.

All these varieties of lard find use in the production of margarine or cooking fats of various types.

Furthermore, the skins of the pigs with the adhering flesh, and the intestines and other parts of the animals which do not yield edible lard, are separately rendered in autoclave digesters and lead respectively to *skin grease* and *yellow or brown grease*; the former may be very pale in colour and form a useful soap-making material, whilst either variety of grease is largely used as a lubricant, e.g. for wagon axles.

Tallows.—The extraction of tallow from oxen or sheep is carried out in much the same way as the production of lard. For edible purposes the fat from the kidneys and related organs, or *suet*, yields the best results. The best edible qualities of tallow are termed “*premier jus*,” and are

obtained by shredding the chilled fat and heating it alone at only moderate temperatures ; tallow for soap-making purposes or when used for candle material is obtained from the remainder of the animals by digestion with water in autoclaves, and is known as *rendered beef* or *rendered mutton tallow*.

Expression of either *premier jus* or *rendered tallow* yields solid *tallow* or *oleostearin* and liquid or greasy *oleo oil* of corresponding quality to the raw material ; the stearin is used in soap- and candle-making, whilst the oil is of value in margarine if of edible quality, or otherwise in low-grade soap and in some types of lubrication.

The bones of the sheep or oxen are worked up separately (frequently in distinct factories) in order to recover the gelatine content as glue, when *bone fat* is obtained as a by-product ; this is a grease suitable in general only as a lubricant and for low-grade soaps.

Wool fat or *wool grease* comes within the present category ; raw wool contains about 20-30 per cent. of fatty and allied matter, which must be removed before the wool can be utilized in the textile industry. The present method consists in "scouring," *i.e.* boiling the wool with a dilute solution of alkali which partly saponifies the fat and removes the unsaponified part as an emulsion with the soap solution. The wash-liquors are collected in tanks and the *wool grease* is removed by skimming off or by passage through a centrifugal separator. Naturally, owing to the regulations affecting the disposal of the waste effluent, this material is available in large quantities ; when of very high quality it is refined and employed under the name of "*lanolin*" as an ointment and skin-dressing, but most *wool grease* is a dark, unpleasant-smelling fat often containing about 30 per cent. of free acids, whilst there is usually also present about an equal proportion of cholesterol and allied wax alcohols. Suggestions have been made to extract the wool with a solvent such as acetone which will remove the fat without adversely affecting the wool fibre ; solvent-extracted *wool grease* should be superior to that obtained by the scouring method.

III. Liquid Fats.—Domestic Mammalian Foot Oils.

(i) *Occurrence.*

Fat.	Source.	Main centres of production.	Technical applications.
NEAT's-Foot (TROTTER) Oil.	Feet of cattle, sheep, and horses.	Europe, Australia, N. and S. America.	Lubricating and high- grade tanning.

(ii) *Average Analytical Characteristics.*

Fat.	Sp. gr. $15^{\circ}/15^{\circ}$.	Ref. index.	Setting pt.	Sap. Val.	Sap. Eq.	Iodine abn. %	Viscosity (Redwood).	Combined fatty acids.	Free fatty acid.		% Unsat.
									Titer.	M. pt.	
NEAT's-Foot (TROTTER) Oil	0.915-0.920	1.468/20°	-4° to +4°	192-197	284-292	67-73	70 secs. at 140° F., 43 secs. at 200° F.	24-27°	28-30°	0-2	0-1% 0.1-0.7%

III. Liquid Fats.—Domestic Mammalian Foot Oils.

—When the hooves of oxen, sheep, or horses are rendered by digestion with water in the course of glue manufacture, etc., a fatty oil is obtained which is termed *neat's-foot* or *trotter oil*. The name refers, strictly speaking, to the oil from the feet of the ox, but is applied commercially at present to the foot oils from various animals.

The oil is produced in considerable quantity and is valued for leather-dressing in the better qualities of leather goods; the highest quality of clear neat's-foot oil, after chilling and separating from deposited solid fats, is a suitable lubricant for delicate machinery such as clockwork, but is increasingly replaced by light petroleum spindle oils. The relatively low iodine number of the liquid neat's-foot oil indicates the absence of even as much unsaturation as that of olive oil, the lubricant properties being therefore accompanied by no tendency to "gum" or thicken owing to atmospheric oxidation of the oil films.

IV. Liquid Fats.—Marine Animal Oils : (a) Fish Oils.—The marine animal oils divide into two classes, those from fish and those from marine mammals.

The true fish oils are characterized by the presence, in addition to oleic and other unsaturated C₁₈ acids, of (i) considerable proportions of acids containing 20 and 22 carbon atoms and possessing unsaturation equivalent to four, five, or six ethylenic linkages, together with (ii) notable quantities of palmitic and hexadecenoic acids and a little myristic and tetradecenoic acids. The liver oils of a few of the fish enumerated below also contain definite amounts of cholesterol and of an unsaturated hydrocarbon, squalene; the latter in rare cases preponderates over the fatty components. The liver oils are also in general conspicuous for their content of the fat-soluble vitamins.

Cod liver oil was largely administered medicinally for many years before its importance as a source of vitamins A and D was understood. It is produced in Norway, in Hull, Aberdeen, and on the north-eastern and north-western coasts of the North American continent by washing

IV. LIQUID FATS.—MARINE ANIMAL OILS: (a) FISH OILS.

(i) Occurrence.

Fat.	Source.	Habitat.	Technical applications.
COD LIVER OIL ..	Gadus Morrhua ..	Northern Atlantic and Pacific Oceans.	Medicinal purposes. Leather industry.
COD OIL ..	" "		
Herring oil ..	Clupea harengus ; C. pallasi	North Sea ; Japan ..	Leather industry.
Salmon oil ..	Salmo sp. ..	North American Pacific Coast ..	Leather industry ; soft soap.
Sardine oil ..	Clupea sardinus ..	Bay of Biscay ; Mediterranean ; Indian Ocean.	" "
JAP. FISH OIL ..	Clupanodon melanostica ..	Japanese coasts ..	" "
MENHADEN OIL ..	Alosa menhaden ..	North American Atlantic coasts ..	Leather industry ; soap ; steel plate industry ; linseed oil substitute (inferior).
Oils from—			
Shark, Basking..	Cetorhinus maximus ..	Japanese seas : Atlantic ..	Leather ; waterproofing.
" Japan ..	Centrophorus sp. ..	" ..	" "
" Moroccan ..	Seymnus sp. ..	Atlantic ..	" "
Dogfish ..	Squalus sp. ..	Atlantic and Pacific ..	" "
Ray ..	Raja sp. ..	" ..	" "

(ii) *Average Analytical Characteristics.*

Fat.	Sp. gr.	Ref. index.	Setting pt.	Sap. Val.	Sap. Eq.	Iodine absn. % °	Combined fatty acids, Titer.	Free fatty acids,		% Unsap.			
								M. pt.	Acid Val.				
Cod LIVER Oil	0.922-0.927/15°	1.480-1.485/15°	Below 0°	182-193	290-308	155-170	17-18°	—	0.5-4%	0.5-1% 1-2%			
Cod Oil ..	0.925-0.940/15°	—	Below 0°	170-180	310-330	130-150	19-24°	—	5-25%	—			
Herring oil ..	0.918-0.939/15°	1.472/40°	—	183-190	295-306	123-146	27-30°	30-32°	2-50	1-25% 1%			
Salmon oil ..	0.925/15.5°	1.478/20°	—	183-186	301-307	130-160	—	26-29°	variable	1-4% 0.5-1.5% 0.5-2.5% 0.6-1.6%			
Sardine oil ..	0.933/15°	1.482/18°	—	186-193	291-301	160-190	28°	35°	4-24	2-12% 5-18% 2-6%			
JAP. FISH Oil ..	0.932-0.935/15.5°	1.481/20°	—	190-196	286-296	150-190	28°	35-36°	10-36	—			
MENHADEN Oil ..	0.929-0.931/15°	1.481/15°	Below 0°	189-195	287-297	160-180	—	—	4-12	—			
Oils from—	Shark, Basking „ Japan „ Moroccan		1.477/20° 1.491/20° 1.486/25° 1.478/20° 1.484/20°		— (350-2240) — (250-330) (300-350)		160-350 — 120-150 140-200		— — 15° 21-24°	— — 20° 28-31°	— — 1-4 2-4	20-90% — 0.5-2% 1-2% 8-30% 1.5-12.5%	
Dogfish Ray ..	0.920-0.930/15°	—	170-175	—	—	—	—	—	—	—			
Ray ..	0.930/15°	—	160-185	—	—	—	—	—	—	—			

the freshly extracted sound livers and heating them under water with open steam, when the oil separates, floats to the top, and is collected, filtered, and refined for pharmaceutical use.

Cod oil is a discoloured inferior oil obtained by similar extraction of diseased livers, or livers which have been stored prior to working up. It is not used medicinally and commands a relatively low price; it is used to a considerable extent in the leather trade for dressing the hides.

Herring oil, *salmon oil*, *sardine oil*, *Jap fish oil*, and *menhaden oil* are produced from the whole fish by digesting them in water with open steam or by expression; in most cases the residual tissues or scrap are dried and used as manure in the agricultural districts near to the reducing factories, in virtue of their high nitrogen and phosphate content.

The oils from all these fish are of the same general composition as and similar to cod oil, and they find similar application in the leather industries. Some of them are also employed in making soft soap, and menhaden oil, in particular, is used as an inferior substitute for linseed oil in the production of linoleum, etc. They are all at present somewhat low-quality oils, although they could probably be produced in the same grades as whale oil (see below), if profitable to do so, by the application of correct methods of extraction. They contain, however, more of the unsaturated acids of the arachidic and behenic series than whale oil, and these, when hydrogenated to a suitable extent to render them adapted for good quality soap, do not lather sufficiently freely to make the use of hardened fish oils attractive.

Of the individual oils, European *herring oil* and *sardine oil* and Pacific *salmon oil* comprise 15–20 per cent. of the whole fish, and are consumed in fairly large quantities by the leather trades. *Jap fish oil* is prepared from fish akin to sardines or small herrings, and exported for the same purpose from Japan in bulk. *Menhaden oil* is the oil of a fish of the herring type which occurs in large shoals off the

North American Atlantic coast, and which is systematically caught and worked up for the oil and for the valuable residual fish manures.

The liver oils of various varieties of the smaller sharks and rays are notable for their high content of the hydro-carbon squalene and, to a less extent, of cholesterol and of certain glycerol mono-ethers of higher fatty alcohols known as batyl, chimyl, and selachyl alcohols ; these oils are not at present available in trade to any large extent.

V. Liquid Fats.—Marine Animal Oils : (b) Mammalian Oils.—*Whale oil* is the most important of this class of fats ; until about 1910 it was merely equivalent to the fish oils described in the previous section in its technical uses, which were mainly confined to the leather industry. The production was, prior to that time, not very large and conducted in a somewhat crude manner, and the oil, usually brownish and evil-smelling, was priced at about £12-£20 per ton.

At the introduction of fat hydrogenation this oil became the favourite raw material for the process in view of its low price and of the fact that, in spite of a general resemblance in composition to the fish oils, its content of acids containing 20-22 carbon atoms is not so great as to render the soap-making properties of the hardened fat very much inferior to those of tallow. This had two consequences : (i) the production of the oil was increased so much that there is some doubt as to whether whales are not in danger of gradual extermination ; (ii) modern methods of extraction were introduced, notably the employment of "mother-ships" fitted with modern rendering appliances which accompany the whaling fleets, and whale oil of extremely high quality, containing less than 0·5 per cent. of free acidity, and almost colourless and odourless on arrival in Europe, came on the market.

The qualities of whale oil at present on the market are roughly as follows :

No. 0 *Grade*, from the first renderings of the blubber when boiled with water in the digesters ; nearly colourless

V. Liquid Fats.—Marine Animal Oils: (b) Mammalian Oils.

(i) Occurrence.

Fat.	Source.	Habitat.	Approximate annual		Technical applications.
			Production.	Imports to U.K.	
WHALE OIL; Greenland or Right	Balaena mysticetus ..	North Atlantic.			
Rorqual or Finner	Balaenoptera <i>sp.</i> ..	Atlantic and Pacific Oceans.	400,000– 500,000	120,000– 150,000	Edible fats and soap (after hydrogenation); soft soap, leather dressing, lubricants.
Bottlenose..	Balaenoptera hypero- odon.	"			
South Sea ..	Balaena australis ..	Southern Atlantic and Pacific.			
SEAL OIL ..	Phoca <i>sp.</i> ..	Most Arctic and Tem- perate oceans.	Consider- able.	—	Illuminant; pharmacy; soap; leather indus- try.
Dolphin oil ..	Delphinus <i>sp.</i> ..	Atlantic and Pacific.	—	—	—
{Jaw oil ..	—	—	—	—	Lubricant.
{Body oil ..	—	—	—	—	Soap, etc.
Porpoise oil ..	Phocaena communis ..	Atlantic and Pacific.	—	—	—
{Jaw oil ..	—	—	—	—	Lubricant.
{Body oil ..	—	—	—	—	—

(ii) Average Analytical Characteristics.

Fat.	Sp. gr. 15°/40°	Ref. index.	Setting pt.	Sap. Val.	Sap. Eq.	Iodine absn. %	Reichert Val.	Combined fatty acids.		Free fatty acids, As oleic acid.	% Unsap.	
								Titter.	M. pt.	Acid Val.		
WHALE OIL: Greenland or Right .. Rorqual or Finne .. Bottlenose .. South Sea ...	0·922-0·926	1·468/40°	Below 0°	188-194	288-298	110-150	1-2	22-24°	25-27°	0·6-20	0·3-10%	1-3%
SEAL OIL ..	0·925-0·930	1·470/40°	-3° to +3°	188-196	286-298	130-150	1-1·5	13-19°	22-33°	2-40	1-20%	0·4-1·5%
Dolphin oil : Jaw oil .. Body oil ..	0·921 .. 0·927 ..	1·452/20° 1·471/20°	-5° Below 5°	270-290 187-220	195-205 255-300	32 100-127	66-110 5-6	— —	— —	2-4 2-12	1-20/ 1-6%	ca. 16% * ca. 2%
Porpoise oil : Jaw oil .. Body oil ..	0·926 .. 0·926-0·937	— 1·462/25°	-16°	250-270 195	205-225 287	30-50 110-120	50-180 11-12	— —	— —	— —	— —	ca. 16% * 2-4%

* Contains higher fatty alcohols ("spermaceti") and lower fatty acids (iso-valeric acid).

and neutral; suitable, after hydrogenation, for edible fats or high-class soaps.

No. 1 Grade, after more prolonged boiling of the blubber with water in open digesters; pale to bright yellow, up to 1-2 per cent. free acidity; suitable, after hydrogenation, for good-class household soaps.

Nos. 0 and 1 Grades are sometimes sold as one grade, No. 0-1.

No. 2 Grade, consisting of the oil obtained by heating the residue from No. 1 grade with water in autoclaves under pressure; yellow or pale brown, up to about 5 per cent. free acidity; suitable, after hydrogenation, for lower-grade soaps or, in its original state, for leather-dressing or in soft soaps.

No. 3 Grade, from the whale flesh by extraction in autoclaves with water under pressure; pale to full brown, usually containing some mucilage, up to 10 per cent. free acidity; more comparable with crude fish oils than the preceding qualities.

No. 4 Grade, by similar extraction of the bones and offal of the whale; a very dark oil liable to contain much mucilaginous matter and up to 30 per cent. of free acidity; the lowest quality of whale oil.

The final residue from the flesh and bones is mixed, ground, and sold as whale guano for manurial purposes.

Seal Oil is not unlike whale oil in chemical composition, but is not produced in such large quantities. It can be hydrogenated and employed in exactly the same manner as whale oil, when available under suitable economic conditions. It was produced, however, in quantity long before whale oil became of such great commercial interest and was on the market in fairly high quality, finding a certain application in pharmacy and a much wider one as a burning oil, especially in lighthouses. The cruder grades are used to some extent in the leather industry.

Dolphin oil and *porpoise oil* are included here because they have also been used to some extent as illuminants and lubricants. Chemically, they are somewhat peculiar,

especially as regards the composition of the oil from the jaws which (like that from the head cavity of the sperm whales, *cf.* p. 154) is quite distinct from the typical oils found in marine animals. The jaw oils contain some 15 per cent. of higher fatty alcohols in combination as wax esters and also considerable proportions of *iso*-valeric glycerides. Lovern has shown that *iso*-valeric glycerides are most prominent in the jaw oils, progressively less so in the head and body (blubber) fats, and that they are practically absent from the liver and other organ fats of the dolphin and porpoise.

WAXES

The waxes are not referred to in this volume at any length commensurate with their scientific interest, because the number which is collected from natural sources for industrial use is not large. It should be borne in mind, however, that the number and variety of natural waxes is probably at least as large as that of the natural fats, although they are not as a rule produced in such abundance.

In the vegetable kingdom waxes are generally found in or upon the outer skin of leaves, stems, flowers and, in many cases, fruit, as well as, to some extent, in the tissues of the leaves, flowers, and fruit. The plant waxes contain as a rule hydrocarbons of the paraffin series C_nH_{2n+2} , where n ranges frequently from about 30 to 60; alcohols of the phytosterol series, either free or combined with fatty acids; and higher aliphatic alcohols of the type of "ceryl" alcohol, $C_{26}H_{53}OH$, or of higher carbon content, again either free or in combination with fatty acids.

Similarly, small deposits of waxes may be found in many parts of animals, and are also present in the cell contents of their tissues; hydrocarbons are not of such frequent occurrence, so far as is known at present, as in the vegetable kingdom, but amongst alcohols there are cholesterol and allied substances, which replace the phytosterols of the plants, and higher aliphatic alcohols sometimes containing fewer carbon atoms than the aliphatic plant alcohols and

WAXES.

I. Vegetable.

(i) Occurrence.

Wax.	Source.	Habitat.	Technical applications.
CARNAUBA ..	Corypha cerifera ..	Brazil	Candles, polishes, lacquers, pharmacy, gramophone records, etc.
CANDELLIA .. (MONTAN) ..	Pedilanthus pavonis .. Lignite and peat ..	Mexico and Texas .. Germany, Ireland, etc..	Polishes, lacquers, etc. Gramophone records, polishes, etc.
Flax ..	Linum usitatissimum ..	Temperate zones ..	—
Cottonseed ..	Gossypium sp. ..	U.S.A., Egypt, India, etc.	—
Seaweed ..	Algae sp. ..	—	—

(ii) Usual Analytical Characteristics.

Wax.	Sp. gr. $15^{\circ}/15^{\circ}$.	Ref. index.	Setting pt.	M. pt.	Sap. Val.	Sap. Eq.	Iodine absn. %	Free fatty acids.	Alcohols + Hydrocarbons.
								Acid. Val.	As oleic acid.
CARNAUBA ..	0.990-0.999	1.472/40°	80-87°	73-86°	79-88	640-710	8-13.6	0.4-7	54-55%
CANDELLIA ..	0.950-0.990	1.456/71°	63-68°	67-70°	50-65	850-1100	12-21	10-20	65-75%
(MONTAN) ..	—	—	—	78-90°	60-105	530-930	10-20	30-70	Ca. 50%
Flax ..	0.963-0.998	—	—	61-70°	80-130	430-700	17-30	24-36	12-28%
Cottonseed ..	—	—	—	66-78°	150-180	350-375	11-13	—	Ca. 50%

of the same carbon atom content (16, 18, 20) as the most common fatty acids.

I. Vegetable Waxes.—*Carnauba wax* is a yellowish brittle material of exceptionally high melting point (83–86°), extracted from the Brazilian palm *Corypha cerifera* (the carnauba tree), on the leaves of which it forms a deposit. The trees are under cultivation and the wax is obtained by cutting the young leaves, drying them and then scraping off the wax powder and clarifying it by plunging into boiling water. After refining and bleaching, either by fuller's earth or charcoal or by a chemical oxidant such as chromic acid, the wax finds employment in many industries, such as in candles, for polishes and lacquers, as a component of gramophone records, duplicating stencils for typewriters, etc. The wax contains minor amounts of hydrocarbons, wax alcohols, and higher fatty acids in addition to higher wax esters of alcohols and acids containing from 26 to 34 carbon atoms.

Candelilla wax, a coating on the stems of the Mexican plants *Pedilanthus pavonis* and other Mexican genera of the Euphorbiaceæ, is extracted commercially by immersion of the plants in boiling water. Although of lower melting-point than carnauba wax, it finds application in similar industries to the latter; it is a brownish brittle mass which may be bleached as in the former case. It consists of hydrocarbons, mainly $C_{29}H_{60}$, $C_{31}H_{64}$, and $C_{33}H_{58}$, together with lesser amounts of wax esters.

Montan wax is a material of high but variable melting point, which occurs in peat and lignite and is extracted therefrom commercially by benzine or similar solvents. The wax is used for the same purposes as carnauba wax. Montan wax from varying sources is of very different composition, but invariably seems to contain esters of an acid $C_{28}H_{56}O_2$, termed montanic acid, and also the free acid. The alcoholic components do not seem as yet to have been clearly characterized; there is always a certain amount of hydrocarbon also present. Some forms of the wax appear to contain alcohols of very high melting point.

Flax wax and *cottonseed waxes* have at present no commercial importance, but are mentioned to emphasize the fact, referred to above, that the characteristic fatty oils of plants are more often than not accompanied in nature by equally characteristic waxes, the latter, however, occurring in various parts of the plant and in relatively minute proportions. Thus *flax wax* occurs to the extent of about 2 per cent. on the seed fibre, and *cottonseed wax* to the extent of less than 1 per cent. in raw cotton fibre.

Seaweed wax has been obtained from deposits of algae which have been converted into an analogous material to peat or lignite, and is said to contain wax esters of higher saturated alcohols and fatty acids of the eicosanic, docosanic, and tetracosanic (C_{20} , C_{22} , and C_{24}) series.

II. Insect Waxes.—Of the numerous insect waxes the only ones of sufficient technical importance to require mention are *beeswax* and *Chinese insect wax*.

Beeswax is collected, probably, more largely than any other natural wax and is used for a wide variety of purposes in polishes, pharmacy, candle-making, and similar trades. It is obtained from the honeycombs (after removal of the honey), either by heating them with water and filtering the melted wax which may be skimmed off, or by pressure extraction. The industry is carried on in many parts of the world and the total production probably approaches about 8,000 tons per annum. Naturally, the waxes from widely different parts vary considerably in texture, colour, and to some extent in chemical composition. Whilst the palest yellow qualities of beeswax are employed directly in many cases, the darker-coloured varieties are more frequently bleached by treatment with bleaching earths or charcoal, or by chemical methods—either simple exposure to air and light, or treatment with ozonized air or hydrogen peroxide; the use of acid oxidants such as chromic acid tends to deterioration of the wax.

Like other waxes, beeswax is somewhat complex in composition and contains about 10 per cent. of hydrocarbons in addition to alcohols, acids, and esters. The wax esters

II. Insect Waxes.(i) *Occurrence.*

Wax.	Source.	Habitat.	Technical applications.
BEESWAX ..	Apis mellifica and other species.	General	Candles, polishes, Pharmacy, etc.
CHINESE INSECT WAX	Coccus cerasiferus ..	Western China ..	Candles, Polishes, etc.

(ii) *Usual Analytical Characteristics.*

Wax.	Sp. gr. 15/15°	Ref. index.	Setting pt.	M. pt.	Sap. Val.	Sap. Eq.	Iodine absn. %	Free fatty acid. Acid Value.	Alcohols + hydrocarbons.
BEESWAX ..	0.962-0.966	1.440/75°	60-63°	63-66°	88-103	540-640	7-14	16-24	48-56%
CHINESE INSECT WAX	0.970	1.457/40°	80-81°	81-83°	78-93	600-720	1-2	0.2-1.5	49-50%

contain a mixture of alcohols of the C₂₄, C₂₆, C₂₈, C₃₀, C₃₂, and C₃₄ saturated series combined with a somewhat similar mixture of the higher saturated fatty acids.

It is the custom in some districts to place artificial combs in the hives, and these are frequently composed of paraffin wax or stearic acid, or a mixture of the two ; the wax from such combs is of course equivalent to a beeswax which has been adulterated with paraffin wax or stearic acid. A method for the approximate detection of adulteration by these or other materials has been proposed by Hübl, following Hehner, who noted that the ratio of the saponification number of the neutral portion of genuine beeswax (*i.e.* wax esters, alcohols, and hydrocarbons) to the acid value (of the free higher fatty acids present) is roughly constant and in the neighbourhood of 3·6-3·8. Consideration of this "ratio number," together with the saponification value of the whole wax and its acid value, may lead to definite indications as to whether the beeswax is genuine, or whether the adulterant is paraffin wax, stearic acid, or other natural waxes of the vegetable series.

Beeswax is one of the waxes most liable to adulteration, and the detection of adulterants in commercial samples is especially important ; for detailed descriptions of the standard analytical methods used for this purpose the reader is referred to the works of Lewkowitsch or Allen (*cf.* Bibliography, p. 184).

Chinese insect wax is the deposit of an insect which is a parasite on certain Asiatic trees, and is somewhat of the type of the European Aphidæ. The industry is peculiar in that the larvæ are deposited on a tree of the privet family, but are removed, hatched out, and cultivated on a species of ash in a distant district ; the wax is deposited on the leaves of the ash trees by the developed insects, and after three months the wax is harvested, first by scraping and finally by boiling the scraped leaves and branches in water.

The wax is pale coloured and consists largely of esters of the higher normal saturated alcohols C₂₈H₅₈(OH),

$C_{28}H_{57}(OH)$, and $C_{30}H_{61}(OH)$ with acids of similar carbon content ; it contains very little free fatty acid. It is employed in the East for much the same purposes as beeswax, and is also exported to a certain extent.

III. Marine Animal Waxes.—The oils from the head cavities and the blubber of cetaceous whales of the genera *Physeter* and *Hyperoodon* (the sperm and bottlenose whales) contain, as alcoholic constituents in addition to or in complete substitution of glycerol, certain saturated and unsaturated higher fatty alcohols containing 16, 18, or 20 carbon atoms per molecule. In consequence, although these oils are usually liquid at ordinary temperatures, they fall within the division of waxes rather than fats and, indeed, on cooling they deposit a solid which is not "stearin," but a material of wax-like properties known as *spermaceti* and consisting largely of cetyl esters of lauric, myristic, and palmitic acids.

The industrial process of obtaining spermaceti consists in chilling the oil for several weeks and then pressing it at the same low temperature (about 0° C.) ; the residual cakes are re-pressed at about 15° C., when more oil separates and the residue is crude spermaceti, which is purified by a third pressing at a somewhat higher temperature. The yield of solid spermaceti is as a rule only 10-15 per cent. of the original oil, since much of the solid wax will remain dissolved in the liquid constituents, whilst the latter, derived largely from the esters of the unsaturated alcohols and acids present, form a large proportion of the original oil.

The unsaturated alcoholic portion of the esters is as susceptible to hydrogenation as the unsaturated acidic part of the molecule, and the unsaturated alcohols are thereby converted into cetyl, octadecyl, and eicosyl (C_{20}) alcohols, so that it is evident that hydrogenated sperm oil is capable of producing far higher yields of spermaceti wax, of higher melting point and harder than the commercial pressed spermaceti.

Sperm Whale Oil is the most valued source of spermaceti and sperm oil : the solid expressed wax is used in candles

III. Marine Animal Waxes (*Spermaceti*).

(i) Occurrence.

Wax.	Source.	Habitat.	Technical applications.
SPERM WHALE OIL ..	<i>Physeter macrocephalus</i>	Atlantic and Pacific Oceans	Lubricant (oil); candles, ointments (spermaceti). Sperm oil substitute.
ARCTIC SPERM OIL ..	<i>Hyperoodon sp.</i>	Arctic Ocean

(ii) *Usual Analytical Characteristics.*

Wax.	Sp. gr. 15/15.	Ref. Index.	Sap. Val.	Sap. Eq.	Iodine absn. %	Combined fatty acids.	Free fatty acid.		Alcohols.
							Titer.	M. p.	
SPERM WHALE OIL:									
Head oil ..	0.881-0.885	1.459/25°	140-144	390-405	60-76	11-12°	13-21°	3-8	1.5-5%
Body oil ..	0.876-0.877	1.462/25°	122-130	430-460	88-93	6-13°	13-21°	2-4	1-2%
ARCTIC SPERM OIL ..	0.876-0.885	1.456/25°	125-130	430-450	77-84	8-10°	10-16°	1.4-3	0.7-1.5%

and in certain ointments, whilst the oil is a valuable lubricant. The oils from the head and from the blubber differ considerably in their composition.

The *head* oil contains the following alcohols in the form of esters : nearly 50 per cent. of cetyl alcohol, about 10-12 per cent. each of an unsaturated alcohol $C_{16}H_{31}(OH)$ and of (saturated) octadecyl alcohol $C_{18}H_{37}(OH)$, about 25 per cent. of unsaturated alcohol $C_{18}H_{35}(OH)$, and the remainder as unsaturated alcohol $C_{20}H_{39}(OH)$. The acids combined with these alcohols and with glycerol in sperm head oil are discussed in the next chapter (p. 174). The oil consists of about 25 per cent. glycerides and 75 per cent. of the wax esters.

The *blubber* oil is less saturated both in its alcoholic and acidic components : the former include about 20 per cent. of cetyl and hexadecenyl (the corresponding unsaturated) alcohols, a small amount of octadecyl alcohol, about 65 per cent. of octadecenyl alcohol, $C_{18}H_{35}(OH)$, and about 10 per cent. of unsaturated alcohols containing 20 carbon atoms. The fatty acids (see this Section, Chapter III., p. 174) resemble those of ordinary whale oil more closely than those of sperm head oil, but are not so highly unsaturated as the former. Sperm blubber oil is made up of about one-third glycerides and two-thirds wax esters.

Arctic Sperm Oil is derived from the bottlenose whale and is very similar in chemical characteristics to sperm oil. The composition of the head and blubber oils has not been investigated in detail of recent years, but the statements in the older literature indicate that they are, like sperm oil, largely composed of liquid wax esters instead of glycerides.

CHAPTER III.—THE CHEMICAL COMPOSITION OF THE MORE IMPORTANT CLASSES OF FATS

It is evident that a full knowledge of the composition of any natural fat involves the following three considerations :

- (a) The quantitative proportions of the various fatty acids which, combined with glycerine, make up the fat ;
- (b) The chemical structure of each of the fatty acids ;
- (c) The quantitative proportions of the actual glycerides present in the fat, *i.e.* the exact manner in which the fatty acids are combined with glycerine.

(a) and (b) The present state of our knowledge of fatty acid structures has been outlined in Section I., Chapter II. (pp. 6–26), and the only reliable methods by which the composition of a mixture of natural fatty acids can be accurately ascertained have been dealt with in Chapter V. of the same section (p. 86).

It must be strongly emphasized that in the absence of definite analyses of this kind statements as to the quantitative occurrence of given fatty acids in fats should be accepted with reserve ; it has not seldom happened that an estimate of fatty acid composition has been arrived at by a comparison, for example, of the iodine absorption and saponification value of fractions of fatty acid, the accuracy of the calculation being vitiated by the presence of other acids of higher and/or lower molecular weight which were overlooked. In other cases insufficient attention was formerly paid to other chemical characteristics of the acids.

The compositions of the fatty acids of fats which have been systematically analysed by modern methods are

therefore the only ones which will be referred to in detail in this work: the fatty acids, separated if possible into saturated and unsaturated portions, are converted into esters which are volatile under highly reduced pressure and are separated by fractional distillation through an appropriate column (Section I., Chapter V., p. 88).

(c) There remains the problem of the manner in which the fatty acids are combined with glycerine, and as indicated in Section I., Chapter III. (p. 29), this may take place in a variety of ways. The general principle of as even (or indiscriminate) distribution of fatty acids as possible throughout the molecules of triglycerides in natural fats (leading to a high degree of heterogeneity in the mixtures of mixed glycerides of which they are composed) has been discussed in Section I., Chapter V. (pp. 92-94), together with the extent to which this principle is followed, and how it may be modified, in different classes of natural fats.

It is now proposed to survey the subdivisions of the fats dealt with in the preceding chapter, to indicate by typical analyses the nature of the component fatty acids present in each case, and to give an outline of the chief component glycerides which occur in each of the fats to be considered. It will be kept in mind, of course, that the proportions of the components of most fats may vary slightly from one crop to another (in the vegetable kingdom), and that somewhat wider variations are to be encountered in animal fats (wherein the diet of the animal and other conditions of its growth may influence the precise composition of its depot or other fats). The data given below for component acids are therefore selected from the available analyses so as to illustrate, when possible, the average or normal composition for each fat.

VEGETABLE FATS

I. Solid Fats.—*The Vegetable Butter Group, including the Nut Oils.*—Reliable analyses are available for most of the fats cited in this group. Typical component fatty acid data (percentages by weight) are given in the following table (p. 159).

	Coconut oil. Per cent. (wt.).	Palm kernel oil. Per cent. (wt.).	Cohune oil. Per cent. (wt.).	Murumuru oil. Per cent. (wt.).	Babassu fat. Per cent. (wt.).	Palm oil. Native (Lagos). Per cent. (wt.).	Plantage (Belgian Congo). Per cent. (wt.).
<i>Saturated acids:</i>							
Caproic, $C_{10}H_{20}O_2$..	Traces	—	—	Traces	—	—
Caprylic, $C_{8}H_{16}O_2$..	7.8	2.7	7.5	6.5	—	—
Capric, $C_{10}H_{20}O_2$..	7.6	7.0	6.6	1.6	—	—
Lauric, $C_{12}H_{24}O_2$..	44.8	46.9	46.4	42.5	45.8	—
Myristic, $C_{14}H_{28}O_2$..	18.1	14.1	16.1	36.1	19.9	1.2
Palmitic, $C_{16}H_{32}O_2$..	9.5	8.8	9.3	4.6	6.9	2.7
Stearic, $C_{18}H_{36}O_2$..	2.4	1.3	3.3	2.1	—	42.5
Oleic, $C_{18}H_{34}O_2$..	8.2	18.5	9.9	10.8	18.1	43.0
Linoleic, $C_{18}H_{32}O_2$..	1.5	0.7	0.9	0.4	—	4.4
<i>Unsaturated acids:</i>							
Oleic, $C_{18}H_{34}O_2$	40.2
Linoleic, $C_{18}H_{32}O_2$	11.2
<i>Saturated acids:</i>							
Lauric, $C_{12}H_{24}O_2$	1.9	—	—	—
Myristic, $C_{14}H_{28}O_2$	3.7	76.6	—	—
Palmitic, $C_{16}H_{32}O_2$	24.4	66.3	10.1	—	—
Stearic, $C_{18}H_{36}O_2$	35.4	1.2	43.3	77	23.7
Arachidic, $C_{20}H_{40}O_2$	—	1.1	5	57
Oleic, $C_{18}H_{34}O_2$	19.3	41.0
Linoleic, $C_{18}H_{32}O_2$	—
<i>Unsaturated acids:</i>							
Oleic, $C_{18}H_{34}O_2$	38.1	26.9	37.4	10.5	43.3
Linoleic, $C_{18}H_{32}O_2$	2.1	—	0.2	1.3	4.3
<i>Chinese vegetable tallow.</i>							
Cacao butter. Per cent. (wt.).
Borneo tallow. Per cent. (wt.).
Nutmeg butter. Per cent. (wt.).
<i>Mowrah butter.</i>							
Japan wax.* Per cent. (wt.).
<i>Shea butter.</i>							
Per cent. (wt.).
<i>Mhanyi tallow.</i>							
Per cent. (wt.).

* Also contains 5.6 per cent. of saturated dibasic acids of the C_{12} and C_{14} series.

The figures in the table illustrate the manner in which seed fats from the same or allied plant families are characterized by the presence of the same fatty acids as major components. The seed fats of the Palmæ are an outstanding instance of this tendency.

Thus coconut and palm kernel oils, etc., contain 45–50 per cent. of combined lauric and usually nearly 20 per cent. of myristic acid, all the other acids (including oleic) being definitely minor components but nevertheless uniformly characteristic in all Palmæ seed fats. The glycerides of coconut and palm kernel oils are consequently a complex mixture. The small proportion of unsaturated acids is present in the form of about 4 parts of mono-“oleo”*-disaturated glycerides to 1 part of di-“oleo”-monosaturated glycerides, and the bulk of the fat (80–85 per cent. in coconut, and 63–66 per cent. in palm kernel oil) consists of fully saturated glycerides containing three saturated acyl groups. In these fats, the component acids of these fully saturated glycerides are in much the same proportion as the whole fat. One lauric radical is probably present in all, or very nearly all, the triglyceride molecules, and a considerable proportion may contain two lauric groups, but trilaurin has never been detected in either fat. Myristic acid will probably occur once in many of the triglyceride molecules, and occasionally twice, but the remainder of the acids will as a rule contribute only one acyl group to any given molecule of triglyceride. Whilst therefore there are undoubtedly many individual glycerides present, practically all of which will contain a lauric group and other two radicals (*e.g.* lauromyristo-olein or caprylo-lauropalmitin, etc., etc.) the most prominent component is dilauromyristin; as a matter of fact, this is the only individual glyceride which has been definitely isolated from coconut or palm kernel oils by fractional crystallization.

Palm oil, from the fruit coat of the oil palm, has quite a different composition from the seed fat. Its main com-

* In this connexion the prefix “oleo” includes linoleic as well as oleic derivatives.

ponent acids are about 40 per cent. each of palmitic and oleic acids, with up to 10 per cent. of linoleic acid. The acids of most palm oils lie within a unit or so per cent. of the figures given in the table, but in a few native palm oils from the western districts of West Africa the content of palmitic acid falls to about 32–33 per cent. whilst that of oleic acid is increased towards 50 per cent. The “even distribution rule” is followed somewhat less closely in palm oil than in most oils, and they contain small proportions (perhaps 5–8 per cent.) of tripalmitin and tri-“olein” (the latter probably linoleodioleins); about three-quarters of the whole fat, however, is made up of “oleo”-dipalmitin and palmitodi-“olein,” with small proportions of “oleo”-palmitostearin (about 10 per cent.) and palmitostearins (about 3 per cent.).

Practically all fruit-coat fats so far studied contain only palmitic and oleic acids as major components, usually accompanied by small proportions of linoleic, stearic, and myristic acids. Two other of these fats are included in the table above, Chinese vegetable tallow and Japan wax. In each of these palmitic acid is the main component, and the “even distribution rule” is largely followed in the glycerides, so that Chinese vegetable tallow contains about 65 per cent. of oleodipalmitin and about 25 per cent. of tripalmitin, whilst Japan wax probably contains over 60 per cent. of tripalmitin and about 30 per cent. of oleodipalmitin; the long-chain dicarboxylic acids of the latter fat are also present as mixed glycerides and confer certain specific physical properties upon it.

Nutmeg butter comes from a member of the botanical family Myristicaceæ, the seed fats in which are almost invariably and uniquely characterized by the presence of large proportions of combined myristic acid.

Cacao butter, Borneo tallow, mowrah and shea butters, and the *Allanblackia* fats are representatives of an interesting group of seed fats from three or four tropical families; the major component acids of these fats are confined to palmitic, stearic, and oleic acids, and stearic acid is typically

prominent in most of them—the only instances in which stearic functions as a major component acid in fats of the vegetable kingdom. In cacao butter, the three acids are present in something approaching equivalent proportions, whilst in *Allanblackia* and some other seed fats (especially those of *Garcinia*) the only major components are stearic and oleic acids, the latter usually forming only about 40–45 per cent. of the total fatty acids. In consequence these fats are comparatively simple mixtures of mixed triglycerides, and oleopalmitostearin and/or oleodistearin are present in large proportions; such fats, therefore, although of comparatively low melting point (e.g. 30–35°), possess a brittleness or "snap" in the solidified state owing to their relatively simple composition. This makes them especially useful in confectionery whilst, from the chemical point of view, they resemble an individual organic chemical compound in physical properties more nearly than any other class of fats. It is important to note that, although some of these fats contain about 60 per cent. of saturated (palmitic and stearic) acids, their content of fully saturated glycerides is insignificant, rarely exceeding 2–3 per cent. of the whole fat.

Cacao butter is made up of about 55 per cent. of oleopalmitostearin and about 20 per cent. of oleodistearin, with minor amounts of stearodiolein, palmitodiolein and oleodipalmitin.

The chief glycerides present in the other fats referred to in this group are as follows :

	Oleo-distearin. Per cent. (mol.).	Oleopalmito-stearin. Per cent. (mol.).	Stearodiolein. Per cent. (mol.).	Palmitodiolein. Per cent. (mol.).	Oleo-dipalmitin. Per cent. (mol.).
Borneo tallow ..	40	30	13	3	8
Mowrah butter ..	Traces	27	30	40	Traces
Shea butter * ..	35	Traces	45	10	Traces
<i>Allanblackia</i> (Mkanyi) fat ..	70	10	18	Traces	Traces

* About 5 per cent. each of palmitostearins and of tri-“oleins.”

The oleodistearin, when isolable in the pure condition by crystallization of these fats, has proved in each case to be β -oleo- $\alpha\alpha'$ -distearin.

II. Liquid Fats.—The "Non-drying" Vegetable Oils.— Typical data for the component acids of fats in this group include the following :

	Olive oil.* Per cent. (wt.).	Ground- nut oil.* Per cent. (wt.).	Almond oil. Per cent. (wt.).	Rice oil. Per cent. (wt.).	Castor oil. Per cent. (wt.).	Rape oil. Per cent. (wt.).	Mustard seed oil. Per cent. (wt.).
<i>Saturated acids :</i>							
Myristic, $C_{14}H_{28}O_2$. . .	1·1	—	1·2	0·3	—	—	—
Palmitic, $C_{16}H_{32}O_2$. . .	9·7	8·3	4·5	13·2	1·1	1	2·0
Stearic, $C_{18}H_{36}O_2$. . .	1·0	3·1	—	1·9	—	1	—
Arachidic, $C_{20}H_{40}O_2$. . .	0·9	2·4	—	0·6	—	—	—
Behenic, $C_{22}H_{44}O_2$. . .	—	3·1	—	—	—	1	—
Lignoceric, $C_{24}H_{48}O_2$. . .	—	1·1	—	0·5	—	1	2·0
<i>Unsaturated acids :</i>							
Oleic, $C_{18}H_{34}O_2$. . .	79·8	56·0	77·0	44·1	Trace	30	24·5
Linoleic, $C_{18}H_{32}O_2$. . .	7·5	26·0	17·3	39·4	6·6	15	19·5
Linolenic, $C_{18}H_{30}O_2$. . .	—	—	—	—	—	1	2·0
Erucic, $C_{22}H_{42}O_2$. . .	—	—	—	—	—	50	50·0
Ricinoleic, $C_{18}H_{34}O_3$. . .	—	—	—	—	92·3	—	—

* These oils were also shown to contain traces (less than 1 per cent.) of hexadecenoic acid.

Olive oils from Italy, Spain, North Africa, Asia Minor, and California have been shown to have compositions not far removed from the typical analysis quoted ; latterly, however, some Italian olive oils have shown a definite departure from this type, their component acids including about 15 per cent. each of palmitic and linoleic acids and only about 65 per cent. of oleic acid. Teaseed oil contains almost the same mixture of fatty acids as that shown in the table for olive oil, and has been used on occasion to adulterate genuine olive oils. The detection of this or other adulterant in olive oil is probably best effected by determining the amount and the iodine value of the unsaponifiable matter : olive oil contains about 1 per cent. of unsaponifiable matter, which is far more unsaturated in character than that of any other vegetable fat, its iodine value being about 200–220. Olive oil may contain small amounts of tripalmitin (about

2 per cent.) and oleodipalmitin, but the bulk of the saturated acids present are in the form of monopalmito- (stearo-, etc.) di-“oleins.” The content of tri-unsaturated glycerides therefore tends towards the minimum and an oil of the acid composition given in the table usually contains only about 60 per cent. of this group, and only about 35–40 per cent. at most of triolein, the rest being linoleodiolein. Olive oils of the type containing only 65 per cent. of oleic acid with 15 per cent. of linoleic acid probably contain little or no triolein and about 40 per cent. of linoleodiolein. The familiar statement that olive oil consists largely of triolein is thus very wide of the mark.

Groundnut oil contains a good deal more linoleic acid than olive oil, and the presence of small proportions of arachidic, behenic, and lignoceric acids in addition to palmitic and stearic is characteristic of this fat. Its glycerides are of the “evenly distributed” class, with negligible fully saturated components, and practically all the saturated acids in the form of monosaturated-di-“oleins” (probably both monosaturated-dioleins and monosaturated-oleolinoleins); tri-unsaturated glycerides form about 45 per cent. of groundnut oil and probably include about 25 per cent. of linoleodiolein and about 20 per cent. of triolein.

Almond oil is also constituted on the usual lines, the small quantity of saturated acids being combined as monosaturated-di-“oleins” and the main components being linoleodiolein (about 50 per cent.) and triolein (about 30 per cent.).

Castor oil, on the other hand, contains substantial amounts (probably over 75 per cent.) of the simple triglyceride of ricinoleic (12-hydroxy-oleic) acid.

Rape and mustard seed oils contain considerable proportions (45–50 per cent.) of the monoethylenic erucic acid, $C_{22}H_{42}O_2$, with oleic and linoleic acids and very small amounts of palmitic and higher (up to C_{24}) saturated acids. Their component glycerides include 45 per cent. (or somewhat more) each of di-“oleo”-erucins and of “oleo”-dierucin (the C_{18} acyl group being either oleic or linoleic),

"Semi-drying" Oils.

	Cotton-seed oil. Per cent. (wt.).*	Kapok oil. Per cent. (wt.).	Sesame oil. Per cent. (wt.).*	Maize oil. Per cent. (wt.).	Wheat oil. Per cent. (wt.).	Sunflower seed oil. Per cent. (wt.).	Croton oil. Per cent. (wt.).
<i>Saturated acids :</i>							
Myristic, $C_{14}H_{28}O_2$..	2·0	—	—	—	—	—	11·3
Palmitic, $C_{16}H_{32}O_2$..	21·2	10·5	9·1	7·8	13·8	3·5	1·3
Stearic, $C_{18}H_{36}O_2$..	1·3	8·5	4·3	3·5	1·0	2·9	0·5
Arachidic, $C_{20}H_{40}O_2$	0·6	1·3	0·8	0·6	0·3	1·0	2·3
<i>Unsaturated acids :</i>							
Oleic, $C_{18}H_{34}O_2$..	29·6	46·1	45·4	46·3	30·0	34·1	55·8
Linoleic, $C_{18}H_{32}O_2$..	45·3	33·6	40·4	41·8	44·1	58·5	28·8
Linolenic, $C_{18}H_{30}O_2$	—	—	—	—	10·8	—	—

"Drying" Oils.

	Soya bean oil. Per cent. (wt.).*	Safflower oil. Per cent. (wt.).	Argemone oil. Per cent. (wt.).*	Hemp seed oil. Per cent. (wt.).	Walnut oil. Per cent. (wt.).	Poppy seed oil. Per cent. (wt.).	Linseed oil. Per cent. (wt.).
<i>Saturated acids :</i>							
Myristic, $C_{14}H_{28}O_2$..	0·3	—	—	—	—	—	0·2
Palmitic, $C_{16}H_{32}O_2$..	9·8	4·2	8·0	5·8	7·0	4·8	5·4
Stearic, $C_{18}H_{36}O_2$..	2·4	1·6	6·0	1·7	1·1	2·9	3·5
Arachidic, $C_{20}H_{40}O_2$	0·9	0·4	—	1·1	—	—	0·6
<i>Unsaturated acids :</i>							
Oleic, $C_{18}H_{34}O_2$..	28·9	26·3	21·8	6·7	19·1	30·1	9·6
Linoleic, $C_{18}H_{32}O_2$..	50·7	67·4	48·0	68·8	65·9	62·2	42·6
Linolenic, $C_{18}H_{30}O_2$	6·5	0·1	0·6	15·9	6·9	—	38·1

	Perilla oil. Per cent. (wt.).	Rubber seed oil. Per cent. (wt.).	Stillingia oil. Per cent. (wt.).	Candle-nut oil. Per cent. (wt.).	China wood (tung) oil. Per cent. (wt.).	Oiticica oil. Per cent. (wt.).
<i>Saturated acids :</i>						
Myristic, $C_{14}H_{28}O_2$..	—	1·2	—	—	—	—
Palmitic, $C_{16}H_{32}O_2$..	7·6	{ 8·3 8·6	6·3 2·8	4·7 4·1	{ 4·6 0·1	11
Stearic, $C_{18}H_{36}O_2$..	—	0·3	—	—	—	—
Arachidic, $C_{20}H_{40}O_2$	—	—	—	—	—	—
<i>Unsaturated acids :</i>						
Oleic, $C_{18}H_{34}O_2$..	3·9	23·6	11·1	27·7	4·1	6
Linoleic, $C_{18}H_{32}O_2$..	44·3	43·3	52·8	41·7	0·6	—
Linolenic, $C_{18}H_{30}O_2$..	44·2	14·7	26·8	21·7	—	—
Elaeostearic, $C_{18}H_{30}O_2$	—	—	—	—	90·7	—
Licanic, $C_{18}H_{28}O_2$..	—	—	—	—	—	78

* Also shown to contain traces (up to 1 per cent.) of hexadecenoic acid.

with subsidiary proportions of monosaturated-“oleo”-erucins.

III. and IV. Liquid Fats.—*The “Semi-drying” and “Drying” Vegetable Oils.*—Typical component acid analyses are recorded in the tables on p. 165.

Apart from traces of hexadecenoic acid (common to all fats), the unsaturated acids of this group of oils belong exclusively to the C₁₈ series. As the proportion of linoleic acid increases the “drying” properties of the oils develop, and reach a maximum when the acids contain little oleic together with much linoleic and also the triethenoid linolenic acid. In linseed and perilla oils the amounts of each of the latter acids approach or exceed 40 per cent. of the total fatty acids. In China wood oil the unsaturated acid is mainly the conjugated triethylenic elæostearic acid, whilst in oiticica oil there is somewhat less of licanic, or 4-keto-elæostearic, acid.

The “drying” oils usually contain only 10 per cent. or less of saturated acids, mainly palmitic and stearic with the former predominating. Some of the “semi-drying” oils contain rather more saturated acids, including 10 per cent. or more of palmitic acid; whilst in cottonseed oil there is over 20 per cent. of this acid.

The glycerides of all the oils listed in the above tables follow the “even distribution” rule closely. Cottonseed oil contains a few per cent. of “oleo”-dipalmitins, but the bulk of the saturated acids are present as monosaturated-di-“oleins,” probably largely palmito-oleo-linoleins; tri-unsaturated glycerides only amount to about 25–30 per cent. of the oil (mainly oleodilinolein with possibly a little tri-linolein). The structure of sesame and soya bean oils has been shown to be similar, the proportions of monosaturated-di-“oleins” and tri-“oleins” (mainly oleolinoleins) depending of course upon those of the component acids in the respective fats.

The component glycerides of linseed oil have not yet been outlined with any precision; but it is probable that about 40 per cent. of it will consist of mixed linoleo-lino-

lenins, the remaining 60 per cent. containing, for the most part, one saturated or one oleic group and two polyethenoid acyl radicals (which may be either linoleic or linolenic). The circumstance that very few of the triglyceride molecules will contain less than two di- or tri-ethenoid acyl groups doubtless contributes to the excellent "drying" properties of linseed oil films. The same general principles probably also hold in the case of perilla oil.

The glycerides of China wood and oiticica oils also appear to be constituted on the usual basis. China wood oil contains a high proportion of the simple glyceride trielæostearin, but oiticica oil (in which licanic acid forms less than 80 per cent. of the total acids) contains but little triketelæostearin and is mainly a mixture of mixed glycerides in which two ketoelæostearic groups are linked with one saturated, or non-conjugated unsaturated, acyl group.

ANIMAL FATS

I. Solid Fats.—*Butter Fats.*—The milk fats from most of the domestic animals are broadly similar in general nature, but are differentiated from all other fats by the presence of butyric, caproic, caprylic and capric acids in definite, if subordinate, amounts. The main component acids are still oleic and palmitic, with subordinate amounts of myristic and stearic acids, minor amounts of lauric and arachidic acids, of an interesting series of lower $\Delta^{9:10}$ -monoethenoid acids of the C₁₀, C₁₂, C₁₄, and C₁₆ groups, and of highly unsaturated C₂₀ and C₂₂ acids. A small amount of diethenoid C₁₈ acid present is not identical with the ordinary linoleic acid of seed fats, although this may be present in traces.

Complete analyses of all the component acids of cow milk (butter) fat are now available, and two typical instances illustrating the normal range of variation are given below. Typical data for other milk fats (in which the minor component acids have usually not all been determined) are also added. Owing to the great range in the molecular weights of the milk fatty acids, comparison by weight

(i) Cow Butter Fats.

		Stall fed (winter). Per cent. (wt.). (a)	Pasture (summer). Per cent. (wt.). (b)	Stall fed (winter). Per cent. (mol.). (a)	Pasture (summer). Per cent. (mol.). (b)
<i>Saturated acids :</i>					
Butyric, $C_4H_8O_2$..	3.7	3.1	9.8	8.5
Caproic, $C_6H_{12}O_2$..	2.0	1.7	4.1	3.5
Caprylic, $C_8H_{16}O_2$..	1.0	0.7	1.6	1.2
Capric, $C_{10}H_{20}O_2$..	2.6	1.8	3.5	2.6
Lauric, $C_{12}H_{24}O_2$..	1.7	3.2	2.0	3.8
Myristic, $C_{14}H_{28}O_2$..	9.3	7.1	9.6	7.5
Palmitic, $C_{16}H_{32}O_2$..	25.4	22.8	23.4	21.6
Stearic, $C_{18}H_{36}O_2$..	10.7	12.5	8.9	10.7
Arachidic, $C_{20}H_{40}O_2$..	0.4	0.7	0.3	0.6
<i>Unsaturated acids :</i>					
Decenoic, $C_{10}H_{18}O_2$..	0.1	—	0.1	—
Dodecanoic, $C_{12}H_{22}O_2$..	0.1	—	0.2	—
Tetradecenoic, $C_{14}H_{26}O_2$..	1.2	—	1.3	—
Hexadecenoic, $C_{16}H_{30}O_2$..	5.0	—	4.6	—
Oleic, $C_{18}H_{34}O_2$..	32.4	41.3	27.0	35.6
Octadecadienoic, $C_{18}H_{32}O_2$..	4.0	5.1	3.3	4.4
C_{20-22} unsaturated	..	0.4	—	0.3	—

(ii) Other Milk Fats.

	Buffalo. Per cent. (wt.). (b)	Goat. Per cent. (wt.). (a)	Sheep. Per cent. (wt.). (b)	Buffalo. Per cent. (mol.). (b)	Goat. Per cent. (mol.). (a)	Sheep. Per cent. (mol.). (b)
<i>Saturated acids :</i>						
Butyric, $C_4H_8O_2$..	4.1	2.1	3.3	10.9	5.6
Caproic, $C_6H_{12}O_2$..	1.4	1.9	2.8	2.8	3.8
Caprylic, $C_8H_{16}O_2$..	0.9	2.7	3.8	1.5	4.3
Capric, $C_{10}H_{20}O_2$..	1.7	7.9	7.8	2.4	10.6
Lauric, $C_{12}H_{24}O_2$..	2.8	3.5	5.4	3.3	4.0
Myristic, $C_{14}H_{28}O_2$..	10.1	10.2	12.2	10.5	10.3
Palmitic, $C_{16}H_{32}O_2$..	31.1	28.7	23.5	28.7	25.9
Stearic, $C_{18}H_{36}O_2$..	11.2	8.1	6.9	9.3	6.6
Arachidic, $C_{20}H_{40}O_2$..	0.9	0.4	1.9	0.7	0.3
<i>Unsaturated acids :</i>						
Decenoic, $C_{10}H_{18}O_2$..	—	0.2	—	—	0.3
Dodecanoic, $C_{12}H_{22}O_2$..	—	—	—	—	—
Tetradecenoic, $C_{14}H_{26}O_2$..	—	0.4	—	—	0.4
Hexadecenoic, $C_{16}H_{30}O_2$..	—	2.1	—	—	1.9
Oleic, $C_{18}H_{34}O_2$..	33.2	31.1	28.3	27.7	25.5
Octadecadienoic, $C_{18}H_{32}O_2$..	2.6	—	4.1	2.2	—
C_{20-22} unsaturated	..	—	0.7	—	—	0.5

percentages is misleading and therefore the molar percentages of each acid are also included. It is then seen that, whilst oleic and palmitic acids are still the main components, butyric, myristic, and stearic acids each contribute something like 10 per cent. to the total fatty acids. In the tables on p. 168, (a) indicates that all minor unsaturated component acids are included, and (b) that these have not been taken into account, in the respective analyses.

It will be noted that sheep and goat milk fats contain larger proportions of capric (and caprylic) acids than cow milk fats, with somewhat less of the C₁₈ acids. The cow milk fats, of which a wide series have now been examined in detail, show a rough balance between, on the one hand, the oleic acid present and, on the other hand, the combined contents of the lower saturated acids; at the same time the palmitic acid content also tends to be slightly less in the milk fats which contain more oleic acid.

The glyceride structure of milk fats is characterized, in the first place, by the presence of 25–40 per cent. of fully saturated glycerides, in spite of the fact that the unsaturated acid content is not unduly low (40–30 per cent.). It is now practically certain that the milk fats are produced in the mammary gland of the animal from glycerides carried to it in the arterial blood stream, and from the above observations on fully saturated glyceride content, together with the unique occurrence of the group of lower Δ^{9:10}-monoethenoid acids (down to, but not below, C₁₀H₁₈O₂), and the effect on the milk fatty acids induced by specific fats ingested in the diet, and by starvation, it is considered probable that the characteristic lower fatty glycerides in milk fats may be produced by transformation in the mammary gland of oleo-glycerides conveyed to it in the blood stream. The mixture of mixed glycerides in milk fat is exceedingly complex, but a recent study (1940) has indicated the presence of the following main groups of components (considered in the categories of oleic, palmitic, stearic glycerides and those of the lower acids of the C_{4–14} series): oleo-mono-C_{4–14}-

palmitins 31-22, oleopalmitostearins 8-17, palmitodioleins 17-4, oleo-mono-C₄₋₁₄-stearins 12-6; smaller proportions of oleo-di-C₄₋₁₄ glycerides, mono-C₄₋₁₄-dioleins, stearodioleins and oleodipalmitins; and fully saturated glycerides (mono-C₄₋₁₄-palmitostearins 9, di-C₄₋₁₄-monopalmitins 7, and small amounts of di-C₄₋₁₄-monostearins, mono-C₄₋₁₄-dipalmitins, dipalmitostearin and palmitodistearin). Nearly 30 per cent. of the fat consisted of glycerides containing one radical each of oleic, palmitic and one of the lower (C₄₋₁₄) acids; nearly 40 per cent. was made up of the four groups oleo-mono-C₄₋₁₄-palmitins, oleopalmitostearins, palmitodioleins and oleo-mono-C₄₋₁₄-stearins; and there was also 19 per cent. of fully saturated glycerides. Palmitic groups were present in about 75 per cent. of the butter triglyceride molecules, and the result of this study is in harmony with the theory of milk fat formation mentioned above.

II. Solid Fats.—Domestic Mammalian Body Fats.—These have been extensively studied in the case of lards and tallow and typical data for the component acids are given in the next table; average figures for both perinephric

	Pig.			Ox		Sheep.	
	Leaf.		Back.	Suet.		Suet.	
	Per cent. (wt.).	Inner. (wt.).	Outer. (wt.).	Per cent. (wt.).	Per cent. (wt.).	External. (wt.).	Per cent. (wt.).
<i>Saturated acids :</i>							
Lauric, C ₁₂ H ₂₄ O ₂	—	—	—	—	0·1	0·6
Myristic, C ₁₄ H ₂₈ O ₂	1·1	1·0	1·3	3·0	2·0	3·0
Palmitic, C ₁₆ H ₃₂ O ₂ ..	30·4	30·1	28·3	29·2	32·5	23·6	30·5
Stearic, C ₁₈ H ₃₆ O ₂ ..	17·9	16·2	11·9	21·0	14·5	31·7	20·1
Arachidic, C ₂₀ H ₄₀ O ₂	—	—	0·4	—	—	—
<i>Unsaturated acids :</i>							
Tetradecenoic, C ₁₄ H ₂₆ O ₂ ..	0·1	0·3	0·2	0·6	—	0·2	0·3
Hexadecenoic, C ₁₆ H ₃₀ O ₂ ..	1·5	2·7	2·7	2·7	—	1·3	1·2
Oleic, C ₁₈ H ₃₄ O ₂ ..	41·2	40·9	47·5	41·1	48·3	35·4	41·4
Octadecadienoic, C ₁₈ H ₃₂ O ₂ ..	5·7	7·1	6·0	1·8	2·7	3·9	2·8
C ₂₀₋₂₂ unsaturated ..	2·1	1·7	2·1	0·2	—	0·8	0·9

(leaf lard, suet) and external tissue (back or rump) fats are quoted for pig, ox, and sheep depot fats.

These fats contain a relatively simple mixture of com-

ponent acids, namely, palmitic, stearic, and oleic acids with minor amounts of myristic and hexadecenoic and traces of other acids. The variation in their properties is mainly conditioned by the relative amounts of oleic and stearic acid present, the combined percentage of C₁₈ acids being usually within the limits of 60–65 per cent. (mol.). Concurrently, the palmitic acid content of nearly all pig and ox depot fats, and those of most other animals, so far examined, lies within the relatively constant limits of 30 (± 3) per cent. (mol.) ; in the fats of lower oleic content, the palmitic acid figure tends as a rule towards the upper limit, and conversely. This approximate constancy, at about 30 per cent. of the total fatty acids, of palmitic acid over a wide range of animal depot fats is remarkable ; but the rule is not without exceptions. It will be noticed that mutton tallow may contain somewhat less palmitic acid, which here may form about 22–25 per cent. of the total acids, and similar figures of this lower order have been observed in one or two other instances, mostly in fats from wild animals. In the opposite direction, Indian beef tallow in which the oleic acid content is unusually low (25–30 per cent.) have been observed to contain up to 40 per cent. of palmitic acid, the amount of stearic acid reaching an apparent upper limit at slightly below 30 per cent.

The foregoing remarks refer to animals fed on a more or less balanced diet, low in fat and fairly rich in carbohydrate and protein. When animals, especially pigs, are given liberal amounts of fatty oil, in the form of oil cake or otherwise, the deposited fat is influenced accordingly and a considerable quantity of the glycerides of the ingested fat may be deposited with the normal depot fat. Thus the octadecadienoic content of pigs receiving soya bean, groundnut, or cottonseed oils has been found to reach values of, respectively, 38, 20, and 27 per cent., with corresponding alterations in the contents of oleic (40, 65, and 32 per cent.) and palmitic acids (14, 10, and 14 per cent.), the linoleic glycerides of the oils being apparently laid down to a large extent in the form in which they were present in the ingested seed fats.

The glyceride structure of the stearic-rich animal depot fats shows a similar departure from the simple rule of "even distribution" to that displayed by the milk fats. A very soft pig outer back fat (containing only 7·6 per cent. of stearic acid in its total acids) only contains about 2 per cent. of fully saturated glycerides, but the amount of these rapidly augments with increasing stearic acid content in the more saturated lards and tallows, and a mutton tallow with 29·3 per cent. of stearic acid contains over 26 per cent. of fully saturated components. This behaviour is readily explicable on the hypothesis that the fat synthesized by the animal from carbohydrate in its diet may be regarded primarily as a mixture of palmitodioleins with smaller quantities of stearodiolein or perhaps triolein, and that these preformed oleo-glycerides are partly saturated or hydrogenated to varying extents before being deposited in the fat reserve depots.

Approximate details are available for the chief glyceride components of pig leaf, inner and outer back fats, and an ox suet fat, and are as follows (molar percentages) :

	Pig.			Ox. Suet.
	Outer back.	Inner back.	Leaf fat.	
Per cent. stearic acid in total acids	13·8	14·4	17·6	22·6
<i>Fully saturated :</i>				
Tripalmitin	1	—	—	3
Dipalmitostearin	2	3	4	8
Palmitodistearin	2	2	5	6
<i>Mono-“oleo”-disaturated :</i>				
“Oleo”-dipalmitin	5	2	9	15
“Oleo”-palmitostearin	27	21	34	32
“Oleo”-distearin	—	—	—	2
<i>Di-“oleo”-monosaturated :</i>				
Palmitodi-“olein”	53	57	40	23
Stearodi-“olein”	7	15	5	11
<i>Tri-“oleins”</i>	3	Traces	3	Traces

The main components in each case are “oleo”-palmitostearin and palmitodi-“olein,” forming together about

75–80 per cent. of the pig fats and about 60 per cent. of the ox suet fat, the amount of "oleo"-palmitostearin and fully saturated components (palmitostearins) showing a general and rapid increase with increasing proportions of stearic acid in the total fatty acids.

Neat's foot oil has been stated by Eckart to contain 17–18 per cent. of palmitic acid, 2–3 per cent. of stearic acid, and 74·5–76·5 per cent. of oleic acid.

IV. and V. Liquid Fats (and Waxes).—*Marine Animal Oils: Fish and Mammalian.*—The fatty acids of the oils of marine animals have received a good deal of attention and data for typical fish, ordinary whale, and sperm whale oil fatty acids are available. It will be recollect ed that the acids of the C₁₈, C₂₀, and C₂₂ series present in these oils are in a state of high unsaturation, and the probable "average" unsaturation of these acids is indicated in each case by the figures given in brackets: the formulæ are given as C₁₈H_{36-x}O₂, C₂₀H_{40-y}O₂, and C₂₂H_{44-z}O₂, and the numbers in brackets are the approximate values of x, y, and z, so far as is at present known.

The figures in the table on p. 174 only refer, of course, to the fats considered in the preceding chapter. Many other fish liver and body oils have been similarly investigated, and the following remarks are based on present knowledge of the group as a whole, rather than on the particular examples before us. The characteristics of nearly all fish and marine animal oil component acids are the presence as major components of unsaturated acids of the C₁₈, C₂₀, and C₂₂, as well as the C₁₈, groups, the high average unsaturation of the C₂₀ and C₂₂ acids, and the presence of only about 15–20 per cent. of saturated acids, of which palmitic acid forms the greater part.

In marine fish liver and flesh fats the amount of C₂₀ and C₂₂ acids, and their average unsaturation, is greater than in freshwater fish fats. The content of C₂₂ acids reaches a maximum in the body oils of the herring family and is somewhat less in liver oils such as that of the cod. The C₁₈ acids amount to 20–30 per cent. of the whole and consist largely

(i) Fish Oils.

	Cod liver. Per cent. (wt.).	Herring flesh. Per cent. (wt.).	Salmon flesh. Per cent. (wt.).	Sardine flesh. Per cent. (wt.).	Menhaden fish. Per cent. (wt.).	Shark liver. Per cent. (wt.).	Dogfish liver. Per cent. (wt.).	Ray liver. Per cent. (wt.).
<i>Saturated acids:</i>								
Myristic, $C_{14}H_{28}O_4$..	3·5	8·0	4·0	6·0	1·0	6·0	4·0
Palmitic, $C_{16}H_{30}O_2$..	10·0	12·0	15·0	16·0	13·0	10·5	14·0
Stearic, $C_{18}H_{36}O_2$..	—	1·0	2·0	1·5	2·5	3·0	—
<i>Unsaturated acids:</i>								
Tetradecenoic, $C_{14}H_{26}O_2$..	0·5	—	—	—	—	—	Traces
Hexadecenoic, $C_{16}H_{30}O_2$..	1·5·5	6·5	10·5	15·5	30·4	10·5	—
C_{18} group, $C_{18}H_{32}-xO_2$..	25(3)	21(4·5)	29(2·8)	24(2·8)	19(10)	24·5(2·3)	20·5(3·3)
C_{20} group, $C_{20}H_{34}-yO_2$..	31·5(6)	28(5·5)	23·5(5·5)	26(5)	16·5(2·2)	29(3·3)	32·5(7·3)
C_{22} group, $C_{22}H_{36}-zO_2$..	14(7)	23(4·6)	16(6·9)	19(5)	12(10)	12(4·0)	18·5(9·5)
C_{24} group, $C_{24}H_{38}O_2$..	—	—	—	—	6	6	—

(ii) Marine Animal Oils.

	Whale.			Sperm whale.			Dolphin.			Porpoise.		
	Arctic. Per cent. (wt.).	Antarctic. Per cent. (wt.).	Head. Blubber. Per cent. (wt.).									
<i>Saturated acids:</i>												
iso-Valeric, $C_6H_{10}O_2$..	—	—	—	—	13·9	3·2	2·5·3	20·8	1·3·6	—	
Capric, $C_{10}H_{20}O_2$..	—	—	3·5	—	—	—	—	—	—	—	
Lauric, $C_{10}H_{20}O_3$..	—	—	16·0	1·0	2·4	1·0	4·6	4·1	3·5	—	
<i>Unsaturated acids:</i>												
Myristic, $C_{14}H_{26}O_2$..	4·1	6·3	14·0	5·0	12·5	7·2	2·8·3	15·8	12·1	—	
Palmitic, $C_{16}H_{30}O_2$..	10·6	18·2	8·0	6·5	11·6	8·6	4·1	7·5	4·7	—	
Stearic, $C_{18}H_{36}O_2$..	3·5	2·4	2·0	—	0·4	0·8	—	0·2	—	—	
Tetradecenoic, $C_{14}H_{26}O_2$..	—	—	—	—	—	—	—	—	Traces	—	
Hexadecenoic, $C_{16}H_{30}O_2$..	—	—	4·0	—	—	—	4·7	3·2	4·6	—	
C_{18} group, $C_{18}H_{32}-xO_2$..	18·4	3·7	14·0	4·0	26·5	25·4	2·7	20·3	4·7	—	
C_{20} group, $C_{20}H_{34}-yO_2$..	32·8(3)	13·3	7(12)	37(2)	15·8(2·8)	24·1(3·3)	2·7	15·2(2·6)	27·2	—	
C_{22} group, $C_{22}H_{36}-zO_2$..	19·3(7)	38·4(2·6)	6(5·2)	12·7(5·5)	18·6(6·5)	4·9(4·9)	1·8(7·6)	16·7(2·8)	10·5(4·8)	—	
C_{24} group, $C_{24}H_{38}O_2$..	1·3(8)	6·3(9·0)	—	2·6(7·2)	5·9(7·6)	—	5·9(7·2)	1·6(4·7)	7·0(4·9)	—	

of oleic accompanied by a tetra-ethylenic C₁₈ acid; ordinary (or seed-fat) linoleic and linolenic acids are not present in detectable amounts. In liver oils of members of the shark and related families which contain relatively high proportions of batyl, chimyl, and selachyl alcohols and/or squalene the average unsaturation of all the unsaturated acids is little more than mono-ethylenic, and small amounts of a mono-ethenoid acid of the composition C₂₄H₄₆O₂ usually appear.

The ordinary whale oils are similar in their component acids to many of the fish oils, but the Antarctic blubber oils, which at present furnish the bulk of the market supply, contain substantially less of the acids of the C₂₀ and C₂₂ groups (and of somewhat lower unsaturation) than oils such as cod liver or sardine oils. This is an advantage technically, the partly hydrogenated C₂₀ and C₂₂ compounds being less suitable in soaps, etc., than those of the C₁₈ group.

The sperm whale oils stand apart in the low average unsaturation of their higher acids, in the comparatively small proportions of these, and (in the head oil) in the presence of considerable proportions of the lower acids lauric, myristic, and tetradecenoic.

Finally, the figures given for dolphin and porpoise oils serve to illustrate what has already been written in the preceding chapter with reference to the relative distribution of *iso*-valeric glycerides in these fats.

The component glycerides of several fish and whale oils have received attention. Some of them have been combined additively with bromine, and some of the bromo-additive products of the glycerides separated subsequently by intensive crystallization. Sperm whale oils contain fairly large proportions of completely saturated wax esters, and isolation and analysis of these has led to some knowledge of their approximate components. Study of the component acids and fully saturated glycerides in cod liver oil and Antarctic whale oil after progressive hydrogenation to a number of stages short of complete saturation has given further insight into the glyceride structure of these oils. All the investiga-

tions in this field point to the conclusion that the fish and whale oils, with their complex mixture of component acids, are made up of complicated mixtures of mixed triglycerides. In any one triglyceride molecule of a fish or whale oil there are probably nearly always three different acyl groups; "even distribution" of fatty acids amongst the glycerol molecules is pronounced, and, coupled with the large number of component acids, leads to a most heterogeneous mixture of, in most cases, trebly mixed triglycerides.

WAXES

Apart from the special cases of marine mammalian waxes (notably the sperm whale oils), the natural waxes, which are found chiefly on vegetable cuticles (leaf or fruit) or are secreted by specific insects, differ fundamentally from the fats. They are mixtures of hydrocarbons, alcohols, and esters of alcohols with acids, all of which are of much higher molecular weight than that (average C₁₆ to C₁₈) characteristic of fats. Nevertheless, they are not, as formerly supposed, derivatives of one particular alcohol and one particular acid, but, in the ester-waxes, include groups of homologues containing even numbers of carbon atoms in the alcohol and acid molecules. The alcohols and acids belong most frequently to the groups C₂₆, C₂₈, C₃₀, C₃₂, C₃₄, and one or other may predominate, but invariably several members, both alcoholic and acidic, seem to be present. The methods of separation which serve for the fatty acids, including fractional distillation of esters, fail to resolve these higher molecular weight compounds, and it is only within the past few years that Chibnall, Piper and co-workers, following the earlier studies of Francis and Piper on the X-ray analysis of normal hydrocarbons, alcohols, and acids of very high molecular weight, have employed the X-ray method to establish the complexity and nature of the hydrocarbons and esters present in many vegetable and insect waxes. It is not, however, practicable or necessary here to deal in further detail with the composition of the natural waxes.

CHAPTER IV.—ATTEMPTS TO PREPARE SYNTHETIC FATTY ACIDS AND FATS

It appears desirable to discuss briefly a variety of attempts which have been made to produce fatty acids and fats technically from non-fatty sources. Proposals of this kind were made originally when petroleum products were very cheap and not in such great demand as at the present time for internal combustion engines; whilst the shortage of fat (and especially of glycerine for explosives) in Central Europe during the war of 1914–1918 caused further interest in the problem.

Synthetic Fatty Acids from Petroleum.—A considerable amount of interest is displayed from time to time in the possibility of producing soap-making material from petroleum, and it is in fact known that fatty acids of sorts can be produced comparatively cheaply from petroleum by processes of oxidation. Such processes were indeed operated to some extent in Germany and Austria during the war of 1914–1918.

It will almost certainly be found, however, that synthetic fatty acids from petroleum will never compete seriously with those from natural fats other than in quite exceptional circumstances due to temporary shortage of the latter.

The petroleum reserves, although very great, have a definite limit, and in view of the enormous and increasing demand for petroleum fuel of various types for power purposes it is unlikely that it will ever prove economical to convert mineral oil on any scale into fatty acids. This argument is reinforced by the consideration that the fat resources of the world are not limited to fixed deposits, but are dependent on recurrent crops, the amount of the latter depending largely on the intensity of cultivation.

Indeed, the contrary process of conversion of fats into hydrocarbon oils by destructive distillation, either as fats or fatty acids, at high temperatures in presence of catalysts such as nickel or some other metals has received investigation. It is suggested that districts remote from oil-fields with abundant natural fat resources (*e.g.* palm oil, ground-nuts, etc., in the tropics, or sunflower and similar annual seeds elsewhere) might obtain motor fuel from fatty materials in this way. Another proposal is to substitute tropical oils such as palm oil, etc., for Diesel oil in engines using the heavier types of fuel oil.

Apart from the economic side of the question, the character of the fatty acids obtained from petroleum presents considerable difficulties : the oxidation processes have not yet been so controlled that any desired mixture of fatty acids possessing properties comparable with those derived from specific natural fats can be produced at will. In view of the complex nature of most petroleum fractions it is difficult to see any likelihood of this being accomplished on any scale, when the problem is regarded from the standpoint of structural organic chemistry.

It is also notable that the most promising of the results already disclosed are from processes in which the relatively costly paraffin waxes are employed as raw material ; but unless the cheap heavy liquid residual oils can be converted into fatty acids as readily as they are transformed by "cracking" into useful motor-fuel oils, the advantage of cheapness of raw material largely disappears.

The earliest attempts to oxidize petroleum to fatty acids were apparently made by Schaal in 1885, who heated paraffin wax with sodium carbonate solution in an autoclave at 170° C. and passed a current of compressed air through the mixture. This process was re-investigated by F. Fischer, who stated in 1920 that oxides of iron, manganese, or copper favoured the process.

Yields of 80-90 per cent. of acidic products are stated to have been obtained, the process occupying several days for completion. The product consisted of a mixture of

acids, somewhat variable in colour, and including considerable quantities of acids containing 13-19 carbon atoms; acids with an odd number of carbon atoms were found to predominate. It appears to have been difficult to control the yield and to prevent too much oxidation, with resulting formation of undesired acids of lower molecular weight.

Other processes have been proposed (Grün, Franck, Kelber, etc.) in which air is blown through paraffins at elevated temperatures in presence of metallic catalysts. The results claimed in the patent literature are reasonably good, but vary considerably: Franck, using air in presence of oxides of lead, manganese, or vanadium, states that 65 per cent. of fatty acids were obtained from a dark paraffin wax, and that lignite oils and tar oils from low-temperature carbonization could also be successfully oxidized; this patentee also found that the acid products give an ester resembling coconut oil when combined with glycol.

It is significant, on the other hand, that Grün, who used a mixture of nitrogen and air to restrain the oxidation, states that his product contained hydroxy-acids, higher alcohols, aldehydes, and ketones in addition to higher fatty acids; whilst Kelber, employing oxygen at 140-150° (in presence of a manganese catalyst), found that a paraffin wax of high melting point (50-51° C.) yielded 40-50 per cent. of higher fatty acids admixed with about 25 per cent. of lower fatty acids and 5-10 per cent. of hydroxy-acids.

It may be added that Harries has patented the application of ozone as an oxidant for petroleum, whilst Zelinski in 1902 suggested that fatty acids might be produced from chlorinated petroleum by the application of the Grignard (magnesium alkyl halide) method. Working costs would appear to preclude either of these processes from competing with simple air-oxidation.

A careful scientific study of the oxidation by air of paraffin wax is due to Francis, who employed a wax derived from Scottish shale oil fractions, 80 per cent. of which, he found, consisted of seven distinct hydrocarbons capable of direct oxidation by air at 100° C. A lengthy period of

induction occurs before appreciable oxidation sets in; but eventually the fixation of oxygen is rapid and exothermic in character. Francis states that, apparently, small amounts of unsaturated substances are produced which act as catalysts (oxygen carriers). The products obtained contained 11-16 per cent. of combined oxygen, but were rather complex in character, although they included considerable quantities of fatty acids which gave soaps in the form of their sodium salts.

From about 1920 onwards, some quantities of commercial fatty acids produced on the Continent by the oxidation of paraffin (petroleum) waxes appeared in this country. An I.G. patent states that oxidation of crude paraffin by air in presence of manganese stearate and sodium carbonate yields 47 per cent. of acids suitable for soap. A specimen of the commercial product examined in 1930 was a cream or pale yellow coloured pasty solid with a definite characteristic odour. It contained about 10-15 per cent. of compounds other than fatty acids, the latter having a mean molecular weight of about 240 and a low iodine value (9). An attempt to resolve the acids by the ester-fractionation procedure disclosed the presence of a wide range of acids, including those containing odd as well as even numbers of carbon atoms, probably of branched chain as well as normal structure in both series, and containing from 8 or less to about 20 carbon atoms per molecule ; probably about half of the material consisted of acids containing fewer than 14 carbon atoms in their molecules. In 1936 a review by Strauss of work in this field since 1933 in Germany, Russia and the United States indicated that the conversion of petroleum waxes to fatty acids was a practical proposition, but that the process would not compete with ordinary fatty acids at the prices then current, but only in the event of a serious shortage of natural fats.

At about this time a new raw material came into prominence, namely, synthetic, mainly straight-chain, higher paraffins (paraffin waxes) produced from carbon monoxide and hydrogen in the course of the catalytic synthesis of motor spirit and lubricating oils from these gases. The

primary objective of this process, due to F. Fischer and Tropsch, was the manufacture from water-gas, or rather "synthesis gas" ($\text{CO} + 2\text{H}_2$), of petrol, Diesel engine fuels and lubricating oils for the motor transport industry. It was found that solid hydrocarbons of still higher molecular weight were also produced and deposited on the catalyst employed, and that the proportion of these obtained could be increased by modifying the conditions of the reaction. Oxidation of these waxes gave fatty acids which were stated to be superior as soap-making materials to those obtained from natural petroleum waxes, and in 1937 it was announced that plants destined to produce 20,000 tons yearly of the synthetic acids were under construction in Germany.

The waxes from the Fischer-Tropsch process are oxidized at about 100° by a current of air in presence of a suitable catalyst (manganese salts); after about 24 hours the material contains 30–40 per cent. of acids, which are removed by soda solution under high pressure at 200° , the non-acidic, incompletely oxidized waxes being mixed with fresh paraffin and re-submitted to the oxidation process. The fatty acids are purified by distillation when, between a first fraction of acids of low molecular weight and a high fraction of acids containing over 20 carbon atoms per molecule (with oxygenated higher fatty acids and a residue of pitch), the acids suitable for soap manufacture are obtained. Jantzen and co-workers have published two analyses of the final commercial products. The first referred to a somewhat crudely distilled mixture, and showed the presence of 7 per cent. of acids of the C_7 series and below, and of 18 per cent. of acids above C_{18} , the intervening 75 per cent. consisting of all the members from C_8 to C_{18} ("odd" and "even") in something approaching similar proportions. Their second analysis was of acids from which the lowest and highest boiling fractions had been separated as described above, and showed traces of C_8 and C_9 acids, 13 per cent. of acids above C_{17} , and 10–14 per cent. each of acids of the C_{12} , C_{13} , C_{14} , C_{15} and C_{16} groups.

It has been stated that the "synthetic" acids marketed for soap production have a setting point of 30°, and a mean molecular weight of 240-250, with a low iodine value (8-10); and that their odour prevents more than 25 per cent. of a soap charge being made up from this source, whilst the radical differences between these fatty acids and those from natural sources demand special technique and skill in processing them into soap. It would still appear that these products will only compete with natural fatty acids, either on technical or economic grounds, when there is a pronounced shortage of the latter. In rational circumstances such shortage is very unlikely to happen.

These synthetic acids can, of course, be converted into glycerides by esterification and are capable of yielding an edible product. The objection of the characteristic odour, due to traces of lower fatty acids, which is valid in their application in soaps, disappears on esterification, since the glycerides of the lower fatty acids are, of course, odourless.

Naphthenic Acids.—The extraction of certain *quasi-fatty* acids, which are present in crude petroleum (*e.g.* from the Russian, Mexican, Texas, and Japanese oil-fields) and whose sodium salts are useful as detergents, may be discussed at this point.

Crude petroleum of the types indicated may contain one or two per cent. of hydrocarbon acids which are extractable by an alkaline solution and have on occasion been isolated thus in technical practice. The recovered acids contain as a rule a considerable proportion of hydrocarbon removed in an emulsified form in the alkaline solution, but furnish sodium salts which are very freely soluble in water and lather abundantly: the admixed hydrocarbon, of course, assists in the production of a free lather.

Whilst the naphthenic acids are thus excellent cleansing agents, their use has not extended beyond the inferior qualities of soaps because they possess a most unpleasant sharp rancid odour, reminiscent of a mixture of crude petroleum and valeric acid.

The chemical nature of these acids is not yet definitely

ascertained, but the work of Aschan, Charitschkoff, and Zelinski goes to show that they are probably derived from cyclopentane and possess the general formula $C_nH_{2n-2}O_2$. Naphthenic acids from $C_7H_{12}O_2$ up to $C_{16}H_{30}O_2$ have been isolated from various petroleums.

Whilst the acids, even when freed from petroleum, are characterized by the unpleasant odour mentioned, their methyl or ethyl esters are pleasant-smelling liquids when purified by distillation in a vacuum. The acids regenerated from the pure esters are mobile liquids, at first with little odour, but the characteristic smell of the crude acids invariably returns after a short period.

Altogether it appears that fatty acids from petroleum are not promising when compared with those from natural fats, except for soaps of low quality as regards colour, odour, and probably detergent power, and except in circumstances of exceptional shortage of natural fats.

Synthetic Fats.—The possibility of producing edible fats from petroleum by combining the synthetic fatty acids with glycerol or other alcohol has also been mooted (*cf.* Franck, p. 179).

The actual esterification of fatty acids with glycerol or glycol is very simple, since it proceeds almost quantitatively when the acids are heated under reduced pressure at 140–180° with a slight excess of the non-volatile alcohol, water being removed as fast as it is formed. This procedure is outlined in the patents of Schlinck, who indicates means by which the tendency of glycerol to polymerization and the production of dark-coloured, viscous condensation products can be restricted.

There is no possibility so far, however, in this process of controlling it so as to produce glycerides of desired constitution (*cf.* Section I, Chapter III., pp. 29–31), and to produce fats of the definite physical characteristics which are desired in edible fats, and which are found ready formed in various specific natural fats.

Replacement of Glycerol in Natural Fats by other Non-volatile Alcohols.—Lapworth and Pearson

showed in 1919 that the glycerol in natural fats can be replaced by carbohydrates such as glucose, or sugar alcohols such as mannitol, when the fats are heated in a vacuum with the alcoholic carbohydrate derivatives. The glycerol distils away and can be collected, whilst the residue is a fatty ester of mannitol or glucose which has a nutrition value of the same order as that of the natural fat.

This again is a process which would obviously only come into use in circumstances, such as war, in which it was urgently desired to use the glycerol for other purposes.

Synthetic Fats from Yeast.—Efforts were made in Germany during the war of 1914–1918 to increase the edible fat resources by utilizing yeast fat. It has been found that the fat-content of yeast is developed considerably when the plant is grown under conditions as favourable as possible to rapid reproduction in media, preferably solid, of low nitrogen content. The expressed fat, according to an examination made by Maclean and Thomas, is a brownish liquid which may contain 25–45 per cent. of non-fatty material, together with glycerides of palmitic, oleic, and stearic acid. Whilst the true fat present is well suited for edible use, the accompanying non-fatty matter would militate against extended use of yeast fat in practice, except under quite abnormal conditions.

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SECTION III.—THE TRANSFORMATION OF FATS FOR INDUSTRIAL USE

Introduction.—Fats may be employed either in the state in which they are produced in nature, or in other cases they may be resolved into their components, glycerol and the fatty acids, and both components may be separately worked up and applied in various ways. Again, by the process of hydrogenation, the character of the natural fat, if unsaturated, may be altered from a liquid oil into a semi-solid paste, a soft or a hard tallow, or even into extremely hard, high-melting, completely saturated fat.

The industrial treatment of fats therefore falls under two headings :

(i) Procedures adopted with the view of purifying or modifying the natural fats, and also of resolving them into glycerol and the mixture of fatty acids which together go to make up the natural esters ;

(ii) Selection of appropriate fats or corresponding component fatty acids, and specific treatments employed to render them available for particular uses.

Whilst the latter subdivision forms the subject-matter of the succeeding sections of the book, the preliminary stages of the industrial treatment of fats are, fundamentally, the same in most cases. It is therefore considered most convenient to deal with these separately in the present section, since not only are the underlying chemical principles the same throughout, but also the proportionate importance of the various operations of fat technology should in this manner be more readily appreciated, whatever the specific use for which the fats or fatty acids may ultimately be designed.

Obviously the first subject to be dealt with is the extraction of the fat from its original source, vegetable or animal ; in other words, the technical separation of the fatty matter from other carbon compounds, cellulose, carbohydrate, protein, etc., which accompany or enclose it in the natural state.

Following this, the processes which are in general use for improving the quality of the crude fats are discussed, including cleansing from mechanically held impurities, the removal of dissolved colouring or odorous material, and the removal of free fatty acid.

Next, a chapter is given to the main outlines of technical fat-hydrogenation, which is usually effected after some preliminary refining of the oil, although further refining may be required subsequently if the hardened fat is destined for purposes such as incorporation in edible products.

Finally, the methods available for resolving the fats into glycerol and fatty acids are considered in so far as they can be handled together and apart from the specific uses of the products ; fat-hydrolysis is referred to again, in the latter cases, in the later sections on soap manufacture, glycerine recovery, candle manufacture, and the application of fats to fibres.

CHAPTER I.—THE EXTRACTION OF FATS

General Principles.—The actual processes employed in the extraction of fats from their natural sources vary according to the type of the latter and must be considered to some extent separately, under the following headings :

- I. Vegetable fats. (a) From fruit pulps.
(b) From nuts and seeds (kernels).
- II. Animal fats. (a) From domestic animals (cattle and pigs).
(b) From marine animals (blubber).
(c) From fish livers.

There are a number of general principles, however, which apply in all cases :

i. The Quality (Freshness and Preservation) of the Raw Material.—The nature of the crude fat obtained after extraction, together with the cost of refining it and the resultant quality of the refined fat, depends primarily and to a very large extent on the state of the raw material when it is worked up. This is a matter which cannot be too much emphasized: the works chemist is frequently called upon to devise methods of producing high quality fat from low-grade crude fat, and this is often a matter of extreme difficulty and uneconomic in practice. The necessity for such procedure should be eliminated as far as possible by strict control of the collection and storage (in cases where the latter is unfortunately essential) of the natural fat-containing material.

Freshly matured natural fats are at their highest degree of purity, *per se*, in the living cell and any subsequent alteration is retrogressive, putrefactive in kind, and possible to avoid by suitable means. Furthermore, traces of nitrogenous and other products of decay, which enter the fat of

stale or slightly decomposed raw material, are almost impossible to remove in their entirety by any economical process of refining, although they are capable, even when present in minute amount, of adversely affecting the flavour, odour, or even the colour of the extracted fat.

In many cases the supervision of the collection of raw material is not easy, especially as regards fruits, nuts, and seeds, when gathered by native or at all events very unskilled labour. The course advised involves the rejection or segregation during picking of individual seeds and fruits which are over-ripe or decaying, and of course the number of these which are needed to provide, say, a ton of fat is enormous. At the same time, this is the only scientific and logical mode of procedure, since it is obviously still more difficult, and in practice quite impossible, to sort out the inferior seed at the extraction factories. Moreover, so far as consignments of material which are transported over a long distance before extraction are concerned, it is evident that the presence of a few decaying units will infect adjacent parts of the stored product and cause progressive deterioration. In this connection attention may be given to the precautions to be taken in the storage of oil-seeds awaiting extraction (*cf. p. 198*).

2. Conversion of the Collected Natural Product into Suitable Form for Fat-extraction.—The physical state of the natural fat-containing material is not suitable for the application of direct extraction, because some or all of the following non-fatty bodies will be found in company with the actual fat :

- (a) Adventitious matter such as sand, earth, and mineral refuse of various kinds in the case of vegetable products ;
- (b) Non-fatty materials as components of the living material adjacent to or present in the fat cells.

In plants these may include hard shells or more fragile husks enclosing seed-kernels, together sometimes with vegetable fibre adherent to the husks, and frequently, a thin inner skin (*testa*) on the actual kernels. The latter, however, is usually not removed prior to extraction.

In animals the fats are closely associated with muscle tissue or other non-fatty cellular tissue, or with the non-fatty parts and skin tissues of the internal organs.

As far as possible the non-fatty portions of the raw material are separated by mechanical processes from the fat prior to the actual separation of the latter, by various means which are indicated later in this chapter. It should be observed that the technology of fat-extraction is as much an engineering and mechanical subject as a chemical problem, and specially designed machinery is available for dealing, not only with the widely divergent types of raw material concerned, but also with different specific varieties of similar materials, such as the oil-seeds. The details of the construction of such machinery are of importance to chemists engaged in particular branches of the industry, but it is not possible here to do more than indicate the general mechanical means which are applied to achieve particular ends essential to the performance of operations on a technical scale in the fat industries. Fuller treatment of the engineering side of the industry will be found in the articles and treatises referred to in the sectional bibliographies.

3. Comminution of the Separated Fat.—When adherent non-fatty tissue, hair, or husks have been removed from the fat it will in general still be present in a form which is unsuitable for immediate extraction, either by reason of its occurrence in too large masses or because, even when sufficiently small, as in sunflower or rape seed, it is enclosed in a covering of thin, hard skin.

Oil-seeds are therefore subjected to a milling process in which the material is shredded into a fine, flaky meal, the fat of cattle and pigs is similarly shredded and minced, whilst blubber fat or livers of marine animals are cut up into small lumps of convenient size to facilitate the removal of the fat from the enclosing cell-tissue.

4. The Actual Fat-extraction.—This is carried out :

- (i) By *expression* in presses, employing at the present day hydraulic power and considerable pressure (p. 202) ;
- (ii) By *solvent-extraction*, the meal or pulp being sub-

mitted to the action of hot petroleum spirit or similar solvent (p. 206) ;

(iii) By *rendering*, i.e. heating the fatty mass, either alone or in presence of water, until the liquid fat escapes from the enclosing cells and floats to the top of the mass.

The choice of method is determined by various considerations with regard to the destined use of the resulting fat, the utilization of by-products, etc., and the guiding principles determining the procedure in the most important classes of fats will be gathered from the details given in the next few pages.

I. VEGETABLE FATS

(a) **From Fruit Pulps.**—The only fats which are at present produced on any large scale from the fleshy parts of fruits are olive oil and palm oil.

The remarks made above with reference to the need of care in collection obviously apply with especial force to these oils, which are obtained from fleshy pericarp and not from hard seeds ; the fruits should be as exactly ripe as possible when gathered. Naturally, also, these soft fruits are more liable to damage by bruising during gathering and transport than nuts or seeds ; the palm fruit, in particular, is liable to suffer during its fall from the tree as well as in transport to the factories.

Extraction is carried out, in the more modern installations, by pulping the fruit (after removal of the kernels in the case of palm oil and of especial brands of edible olive oil) and then expressing the oil by the application of hydraulic pressure in similar plant to that employed for pressing oil-seeds (see below, p. 202) ; special depericarping machines are frequently employed in the palm-oil factories, consisting of two horizontally and oppositely rotating discs carrying curved radial abrading edges, the action of which on the fruits fed into the machine is to strip the pulp completely from the kernel-shells and eject the latter through holes in the peripheral casing, whilst the pulp flows outwards also and is run off in a heated trough to the presses.

In modern practice the ripe, undamaged palm fruit is sterilized prior to extraction by heating under slight steam pressure. It is then either passed through a depericarping machine and the pulp fed into a steam-jacketed cage press and subjected to hydraulic pressure, or else the whole fruit is passed to a digester, in which the pulp is removed from the kernels and then passes into a centrifugal extractor so fitted that steam can be injected into the mash during centrifuging. Both presses and centrifuges find use in modern plantations. The overall yield of the oil on the fruit (85–88 per cent.) and the working costs are much the same. The centrifugal process gives a slightly lower oil-yield than extraction by pressure, but produces a cleaner oil which suffers less loss during subsequent purification. The time of actual extraction of the oil in the centrifuge is only 15 minutes and this tends to minimize free acidity in the palm oil produced. The old system of transport of palm oil in wooden barrels is replaced by the use of steel drums, and in some instances the oil is now shipped to Europe in vessels fitted with large oil-tanks.

The production of olive oil has also been much improved. The fruits are broken up in stone edge-running mills and the pulp (with seeds) placed in specially constructed iron cage presses or fed continuously into a machine constructed similarly to an "expeller" press (*cf.* p. 205). There is alternatively a centrifugal process, in which the pulped fruits are first of all pressed through wire screens to remove the seeds, the pulp then being centrifuged. By either of these three modern methods, 60–70 per cent. of the oil present is recovered in first-grade quality in one operation; second-grade oil is obtained by solvent extraction of the residual marc.

Appreciable amounts of mucilage and vegetable tissue may escape into the oils from the pulp during pressing: these are separated by settling the oil in tanks, either alone, or after boiling with water or brine, or injecting a current of steam. The clear oil is subsequently drawn off from above the settling.

(b) **From Nuts and Seeds (Kernels).**—This is by far the most frequent source of vegetable fats, and the processes of extraction will now be considered in more detail with particular reference to oil-bearing seeds and nuts.

For the purpose of description we may include consideration of the extraction of coconut, palm kernel, ground-nut and cottonseed oils, and of soya bean, sunflower, linseed and rape oils.

The procedure adopted varies in many details ; in the first place we may note that coconuts (copra), palm kernels, groundnuts, and cotton seeds are "oil-rich" and contain over 40 per cent. of extractable oil in contradistinction to the remainder, whose oil-content is about 20 per cent. This causes certain differences in detail of method, since it is very desirable not to cause any efflux of oil from the seeds during the preliminary processes of cleansing and milling, in order to avoid clogging of the meal during the subsequent actual extraction.

Further, the residual seed-cake is a by-product second only in importance to the oil itself, owing to its ready disposal as a cattle food ; this leads to the following considerations :

(i) Certain seeds contain substances of a glucosidic or even alkaloidal nature which are poisonous to cattle, and therefore the seed-cake is useless except as an artificial manure, for which the available return is only about a quarter of the value as cattle food : it is probably owing to this fact that certain abundant tropical fats such as mowrah butter and shea butter have not yet come into very extended use.

(ii) Precautions have to be taken to guard against the admission into cattle-cake of sharp husks or shell fragments, or of vegetable fibre of a thorny nature (which occurs on some seed-husks) or other material which would injure the cattle.

(iii) Cattle feeding cake is of two main kinds, the straight oil-cake which is valued upon its oil content, and "compound" cakes which are composed of seed-cake poor in

oil admixed with molasses or starchy material so as to give a cake of high carbohydrate content.

The demand for the cakes has an important bearing on the choice of method of extraction—pressing leaves about 6 per cent. or more of oil present, whereas by solvent extraction the oil content can be diminished to about 1 per cent., and the residue is only suitable for “compound” cakes.

Seed Collection and Storage.—The paramount importance of this aspect of fat-production may be further illustrated by individual reference to the oils enumerated on p. 196.

Coconut oil is extracted to some extent from fresh nuts in factories near the plantations, but to a much larger extent by pressing the exported “copra,” which consists, as stated on p. 112, of the fleshy matrix of the ripe coconut, which has been removed from the hard shell and dried by exposure to air and sunlight—a process in which there is considerable opportunity for hydrolytic and putrefactive decomposition unless due care is exercised. This process, however, when properly carried out, leads to a better grade of coconut oil than is obtained by the alternative process of heat or kiln drying, in which the copra is dried on a grille of bamboo over the heat from burning coconut shells. Kiln-dried copra is still produced in fair quantity, but the sun-drying process is increasing in use; the kiln-dried product is liable to be dark coloured and to suffer in odour and taste from its exposure to smoke.

Palm kernels are mainly obtained by hand-breaking of the palm nuts after removal from the fruit pulp; the nut is very tough and difficult to break mechanically without damaging the kernel, so that the operation is often performed by native manual labour. In consequence a certain amount of mineral and vegetable matter is apt to become adherent to the kernels. Machinery wherein the shells are cracked by impact in a rapidly rotating cylinder against rigid metal teeth is also used to an increasing extent.

Groundnuts are extracted both in their husks and without; in the latter case the husks are frequently removed

by machinery before shipment from West Africa, etc., and it is found that the decorticated or shelled nuts do not as a rule yield oil of such high quality as the undecorticated nuts. Obviously decomposition sets in more readily during storage of the kernels unprotected by their husks.

Cotton seed is coated with a short fibrous hair in addition to the long cotton fibre ; that occurring in the Egyptian and Indian varieties is much less in quantity, almost non-existent, but the seed contains more colouring matter and is also more liable to hydrolytic decomposition, so that crude Egyptian and Indian cottonseed oils, especially if exported prior to extraction, are usually darker in colour and more difficult to refine than the American oil.

Soya beans are enclosed only in a thin, tight skin, which if ruptured or punctured leads to putrefactive decomposition of the seed, the deterioration rapidly spreading to adjacent seeds.

The smaller seeds of *sunflower*, *flax*, *rape*, etc., are equally liable to deterioration unless gathered, ripened, and dried correctly before storage ; another point in the gathering of seed from small annuals such as the flax and *Brassicæ* is the care necessary to ensure that seeding weeds of similar stature, and sometimes also similar habit, are as far as possible excluded from the crop.

The *storage* of any and all of these seeds, which may be a matter of a considerable length of time in the case of annual crops which mature at one point of the year and cannot be extracted other than over the whole year, also demands considerable care. The most modern method is to effect storage in long, narrow, well-ventilated bins with vertical walls ("silos"), from which the seed can be discharged by its own weight on to a band conveyor. The temperature of the seed in each compartment is carefully watched, and if it tends to rise, indicating the onset of hydrolytic decomposition, the seed is transferred from one bin to another in order to remove the heat and thereby check the progress of incipient decay.

Of course, as far as possible the seeds are worked off

with a minimum of delay, but for the reasons just indicated storage for a shorter or longer period cannot be avoided.

Naturally the kernels of seeds with a hard, loose protective coating (husk or hard shell) store best in the shells so long as these are whole ; but on the other hand, considerations of economy in transport tend to cause imported seed to be shipped in many cases in the decorticated state. Thus the shell of the palm fruit weighs about three times as much as the kernel, whilst even the groundnut husk, which is thin and encloses a bulky kernel, weighs about 30 per cent. of the whole nut.

Seed cleaning.—Mechanically adherent mineral or vegetable matter is removed from the seeds in the first stage of their passage from the store to the extractors by a combination of shaking and screening machinery.

The seed, more especially if it is of a large or nut variety, is first of all passed through a "tumbler" (an open revolving cylinder set at an inclined plane) or over a series of shallow steps in order to cause the individual seeds to rub against each other and dislodge the adhering foreign matter.

It may then pass over a rough screen sufficiently coarse in mesh to allow all the seed to pass through, but on which any large pieces of foreign material are retained ; it may subsequently be screened from fine dust, etc., by passing over a shaking tray screen or through a rotating cylindrical screen or screens of such sizes that the seed is separated from all foreign matter other than particles of magnitude between the extreme limits of the diameter of the seeds.

Before passing on to the milling or decorticating processes the cleansed seed is passed over a magnetic separator in order to remove small particles of iron which may have escaped separation in the cleansing process ; this is an important precaution, both in view of danger to cattle from the presence of fragments of iron in the seed-cake, and also in view of possible damage to the cutting and crushing roll machinery in the succeeding processes from the same cause.

Delinting.—American cotton seed and a few other seeds which possess a thick growth of short fibrous hairs on the

seed-cortex are frequently subjected to a process which removes the latter prior to extraction of the undecorticated seed.

It should be noted that there is a certain demand for oil-cakes in which the fibrous matter is present, especially in extracted cakes which are to be compounded with molasses, when the fibre or lint acts as a binding agent for the latter.

On the other hand, the presence of the cottonseed husks in the extracted meal finds favour with some consumers, and for this purpose undecorticated seed is extracted after the fibre has been removed.

In this case the fibre-covered or woolly seed is first of all delinted by mechanical or chemical means.

The mechanical methods consist of pressing the hulls through a series of rollers covered either with knife-edges, or roughened similarly to a nutmeg grater, or, for closely adherent fine fibre, provided with carborundum surfaces. The rolls are carefully spaced so that the largest hulls present are, as far as possible, not cut or broken, in order to prevent exudation of oil at this stage.

Another method which is largely employed is to steep the hulls in dilute sulphuric acid for some hours, subsequently washing in water and drying. The acid treatment loosens the fibre from the hull so that it can easily be detached by gentle mechanical rubbing and separated from the delinted hulls, for example by winnowing in a current of air provided by suction-fans or blowers.

Decorticating.—When it is not desired to have the ground husks present in the extracted meal, the seed kernels are separated from the hulls by suitable decorticating machines. These consist generally of a double or treble system by means of which the larger seeds are treated before the smaller ones. Decortication is effected by passage of the seed between rollers carrying cutting edges or sharp grooves which are intended to break the shells without crushing or cutting the kernel or "meat" beneath the latter.

In the double huller process the seed first passes through

a machine set to deal with the larger seeds, the emerging material consisting of untouched small seeds, decorticated kernels from the larger seeds, together with broken hulls and a small amount of powdered kernel; passage over a shaking screen removes the decorticated whole kernels (which are ready for milling), whilst the remainder passes to a "beater" in which the powdered kernel or "meat flour" is sieved from the mixture of broken shells and untouched seed. The latter mixture is then passed into the second "huller," which is set to deal with the smallest seeds present, after which a similar procedure is followed, the whole kernels being separated in a shaker, and the hulls passed through a second beater to remove all the meat flour.

The whole kernels and meat flour are conveyed together to the mills, whilst the hulls are disposed of separately.

It must of course be understood that the whole of the transport of the seed in these preliminary processes is as far as possible mechanical, and the plant should be designed to take advantage of gravity feed where possible between the warehouse and the actual mill. The seed is transferred in closed belt conveyors supplemented where necessary by shallow pan or bucket conveyors for lifting the seed. Due precautions are necessary to guard against the possibility of fire or explosion at points where there is any considerable production of fine dust from the husks or meats.

Milling.—The conversion of the prepared kernels into a form sufficiently fine for efficient extraction is again carried out by passage through a series of cutting rolls. Except in the case of very fine seeds of relatively low oil content, rolls which have a cutting rather than a crushing action are used, as it is desired to obtain the meal in a fine condition without actually forcing oil from the cells, which would result in clogging of the rolls and also in inefficient subsequent extraction of the meal.

For coarse seeds the rolls may be fluted, for fine seeds the corrugations are very fine or non-existent.

Two classes of crushing-machine or rolls are employed, "reducing" and "finishing." The reducing rolls are

employed for preliminary breaking down of the larger seeds such as copra, palm kernels, and groundnuts, and consist of two, three, or four pairs of rolls through which the seed is successively passed. By this means it is broken down into fragments sufficiently small to be dealt with adequately in the finishing rolls.

The smaller seeds, including cotton seed, linseed, and rape, only require passage through the finishing rolls. These are more exclusively crushing rolls, and usually consist of a series of five superimposed heavy smooth steel rollers. The seed passes through the series in a downwards direction and is thus submitted to four successive passages through the rolls, each one being at a higher pressure than the one preceding owing to the increasing cumulative weight of the rolls above the seed.

Correct milling is essential to high efficiency of oil yield, especially in modern hot-pressing, and much ingenuity has been expended by the engineering trade on designing crushing machinery which will produce seed-meal in even fine particles of a flaky nature without actual expression of oil (*i.e.* undue rupture and abrasion of the oil-bearing cells). The meal is transferred as rapidly as possible, and preferably by gravity feed (in conveyors either of the bucket or of the Archimedean screw type, in order to minimize rubbing and abrasion) to the extraction vessels, the action of which is described below.

Extraction by Pressure.—This system is generally favoured as yielding the highest grades of oil, since minor amounts of non-fatty material are less readily abstracted from the seed by pressing than by the application of solvents, and there is no question of the presence of traces of solvents left in the finished oil. At the same time, the modern solvent-extraction processes yield in many cases oil very little inferior in quality to pressed oil, consume much less power, and are cheaper in labour costs. As already indicated, the determining factor in the choice of mode of expression is very frequently, at the present time, the use to which the residual cake can be put for feeding purposes.

In cold-pressing the meal is packed directly into the presses, but for hot-pressing a further intermediate stage is requisite between the finishing rolls and the presses, namely, "cooking."

This is effected in steam-jacketed closed vessels provided with mechanical stirring gear, into which the meal is charged and warmed up carefully with slow agitation to about 50–60° C.

It may here be interpolated that the amount of moisture present in the seed during "cooking" has an important effect on the subsequent expression of oil. For extraction in hydraulic presses, a moisture content of about 7–9 per cent. in the meal usually gives the best results, but the optimum proportion varies to some extent with the oil-seed concerned.

On the other hand, the Skipin process depends on the discovery that oil seeds, when ground and moistened with a definite proportion of water and heated to a moderate temperature, yield up their fat more readily and completely. Indeed, a considerable proportion of the oil separates from the meal during the process and may be removed, for example, by centrifuging, after which the residual meal is dried somewhat and the remaining oil recovered by pressure or by solvent extraction. The optimum moisture content varies with different seeds, but is usually between 15 and 20 per cent. The optimum temperatures vary more widely, e.g. 60–85° for sunflower or castor seed, 68–72° for cotton or hemp seed, 35–37° for sesame and groundnuts. Goldovski suggests that the effect is due to the breaking down of oil-protein complexes by the moisture, with liberation of physically free fat.

The procedure proposed by Beckmann, namely, to ferment oil seeds with *B. Delbrücki* which contains proteolytic enzymes, appears also to depend on the liberation of fat by partial removal of the attached protein. It has been shown that some, but not all, oil seeds yield their fat more completely after fermentation in this way, but the process is not, so far as is known, used technically.

In either cold or hot pressing the process may be carried out in plant of a variety of types ; the pressing industry has developed very considerably in recent years and much higher pressures are now in general use than was the case formerly. The description given here is restricted to a general indication of the most modern practice.

The hydraulic press-casing is generally set vertically, pressure being applied by forcing a ram upwards from the hollow base of the press. The horizontal cross-section of the press is rectangular or square and of dimensions which will yield a residual cake of convenient size for handling, e.g. about 14 by 20 inches.

In "open" types of press the seed-meal is fed into bags of filter-cloth which rest between horizontal iron plates. In the "closed" type the use of cloth may be dispensed with, and the meal is filled direct on to horizontal iron plates closely fitting the inner casing. The inner vertical casing of the closed press is covered with minute perforations about 0.03 inch in diameter, through which the exuding oil is discharged and runs away in the space between the perforated inner casing and the outer shell of the press. In this system the requisite amount of meal (either cold, or from the cooker) to give a residual cake of definite size is fed on to one of the horizontal plates, another plate is inserted, and so on until the press is filled.

Pressure is frequently applied in two stages : the greater part of the oil is removed at a lower pressure than the final portions, and usually about $\frac{1}{2}$ - $\frac{3}{4}$ ton per square inch is employed initially. This causes liberation of oil until the residual meal-cake contains perhaps 12-20 per cent. of oil, depending on the nature and oil content of the original seed. The next stage consists of the application of a much higher pressure—3 or 4 tons per square inch in a closed press, or $1\frac{1}{2}$ -2 tons per square inch in the open type—when further oil is removed and the oil content of the cake may be reduced to 5 to 6 per cent.

The actual oil content left in the cake is adjusted over the range of 5-10 per cent., to suit the demands of the

straight cattle-cake market ; the quality of the oil obtained by extraction at the higher pressure is not always quite equal to that of the first runnings from the first stage of the process.

Pressing machinery designed by different makers varies in detail, apart from whether it is of the "open" (or Anglo-American) or "closed" type ; in modern practice it is usual to have separate installations for high and low pressure, the cage of cakes being removed by machinery from the low- to the high-pressure ram.

The cost of installation of the hydraulic pressure extraction system and the necessary accessories, including hydraulic power, considerably exceeds that of a solvent-extraction plant of the same oil capacity, whilst the pressure system requires nearly twice as much man-power for labour as the extraction method ; nevertheless, it has the advantage of yielding directly a compressed cake of suitable oil content for cattle and also, in most cases, the oil produced by pressing is held to be superior to that obtained by the use of solvents.

The expressed oil contains a little mucilage and occasionally a little escaped meal which is, however, readily separated by the methods indicated in the next chapter (p. 218).

Extraction by "Expellers."—In 1903 Anderson invented a screw-press for the continuous extraction of oil from seeds by pressure which has become known as an oil-expeller. This machine has been developed and at the present time a considerable amount of oil seeds are crushed in modern forms of the original Anderson expeller. The general principle of the machine is that of a screw conveyor. Either a screw of constant diameter operates in a box (pierced with small holes) which narrows progressively towards the exit end, or the surrounding perforated box is cylindrical whilst the diameter of the screw shaft increases towards the remote end. In both cases, of course, the action of the screw causes increasing pressure on the meal as it passes through the expeller.

The expellers are usually constructed as self-contained units, each with its own heating kettle for preliminary

"cooking" of the ground meal. They operate continuously and have proved useful both for small and large outputs. There is naturally considerable strain on the screw-conveyor mechanism which is constructed of specially resistant steel. Furthermore, the frictional heat liberated causes the meal to become hotter as it passes through the expeller; careful regulation of the moisture content of the meal and of its cooking in the heating kettle is essential to the efficient working of the process.

The expeller principle is a useful adjunct, with oil-rich seeds such as copra or groundnuts, prior to their treatment in hydraulic presses or by solvent extraction; preliminary passage through an expeller reduces the oil content to a stage at which the material is more amenable to high pressure or solvent extraction. On the other hand, the whole treatment of the seed can be carried out in the expeller, and the oil content of the residual meal reduced to 5–6 per cent., *i.e.* the normal content of oil in expressed oil cake. Groundnuts or cotton seeds will normally be thus completely expressed in two or three stages, or passages through the oil expeller.

The oil expeller can be employed with most seed meals, and is frequently used on the large scale for cotton seed, groundnuts, castor seed, and tung seeds. The expressed oil meal is produced as a compact cake which is flaked off by a conical projection mounted at the discharge end of the box in which the screw conveyor operates. Separate types of expeller are designed to operate at relatively low pressures (to remove a portion of the oil present in the seed) and at high pressures for the production of oil cakes containing only 5–6 per cent. of residual oil. Expellers are available to deal with up to 100 tons of seed per day of 24 hours.

Solvent Extraction.—Many of the more volatile organic solvents have been proposed as technical solvent media for fats, but at present the choice lies in practice between petroleum spirit (benzine) and trichlorethylene (Westrosol).

Petroleum spirit, b.p. 60–80° C. or b.p. 80–100° C., is probably most widely used. It has the advantages of

cheapness, easy removal of its last traces from the extracted oil, and probably a minimum tendency to dissolve non-fatty organic matter present with the oil in the seed ; its only disadvantage is its extreme inflammability.

Trichlorethylene is non-inflammable, can be removed from the extract as readily as petrol, and does not as a rule dissolve non-fatty material to a notably greater extent than the latter ; it is, however, much dearer than petrol, and objections have been raised to it on the score that it is liable to some decomposition in presence of steam, when hydrochloric acid and undesirable organic chlorine compounds are produced. It is fair to add, however, that the latter trouble is stated to have been due to imperfections in the manufacture of the solvent, now overcome, and that pure trichlorethylene is stated to be completely stable under the conditions of use ; this is borne out by the high quality of many samples of oil extracted on a technical scale by this solvent.

The seed is generally not milled quite so finely as for pressure extraction, but equal care must be taken to have the meal as nearly as possible even in size of flake and to prevent exudation of oil in passage through the rolls, in order to prevent channelling of the solvent in the extractors with uneven extraction of the oil.

The process is usually carried out in a series of large vessels and by a modified form of what is known as the counter-current principle. This depends on the obvious fact that it is easiest to dissolve a substance from a mixture in which it is present in the relatively largest quantities. For example, in scrubbing a gas with water to remove, say, ammonia, it is most efficient to cause the gas and the water stream to move in opposing directions, so that the crude gas most highly charged with ammonia first of all meets water which already contains ammonia removed from earlier portions of the gas, whilst the fresh water meets gas which has already been subjected to the action of considerable water and is thus denuded of all but the last traces of matter soluble therein.

It is found that this leads to a minimum consumption of solvent per unit of solute extracted, but in the case of oil-seeds it is usual not to operate the system continuously, but in an intermittent or batch form. The meal is charged into cylindrical vessels, closed except for a reflux condenser, and four or more in number; sometimes fibre mats are interposed between every foot depth or so of the meal in order to minimize tendency to channelling or short circuiting of the solvent. The fresh meal is first of all exposed to the action of solvent which has already been in contact with a number of batches of partially extracted meal, and successively, afterwards, to batches of solvent which have been less frequently used, until finally it receives a charge of fresh solvent.

The solvent is usually employed first cold and subsequently in a warm condition, and the temperature of each extract is maintained at a suitable point below that of free ebullition. The fat-saturated solvent is finally passed through a double still system. In the first phase of the stilling process it is heated by closed steam coils and removal of the bulk of the solvent from the extracted oil is effected, the solvent vapours being passed through efficient condensers and recovered for further use. The oil from this first or "stripping" still passes to the top of what is in effect an ordinary plate fractionation column at the base of which steam is admitted, when the oil, exposed in thin films as it descends the plates of the column to the current of steam emerging from the domes on the plates, is completely freed from all traces of volatile solvent. The oil is drawn off at the bottom of the "finishing" still, settled and purified from traces of mucilage, etc., as in the case of pressed oil.

The residual meal in the extractors, which will contain only about one per cent. of oil, is steamed and then transferred by hand or by gravity to a drier, in which the moisture content of the extracted meal is reduced to about 10 per cent.

As already stated, the oil yield by solvent extraction is very high, whilst the loss of solvent is very small and should not exceed 3-5 gallons of spirit per ton of oil extracted.

In order to minimize loss of solvent any air or uncondensable gas escaping from the solvent-recovery condensers is usually scrubbed through oil-washers or passed over an adsorbent material such as charcoal or silica gel.

Residual Oil-cake.—A considerable amount of attention has already been paid to this product throughout this chapter, but it is convenient at this point to summarize the outlets for the material and indicate its range of composition, since it will then not be necessary to re-open this aspect of the fat industry later in the course of this volume.

As already stated, fully extracted oil-cake has at all events considerable value as an artificial manure, in virtue of its content of protein nitrogen, phosphates, and potash, assuming that there are agricultural districts in sufficiently close proximity to the extraction factories to prevent the cost of transport rendering its use uneconomical as compared with that of other local fertilizers more readily to hand.

The market value of the cake is, however, many times greater if it can be sold for incorporation in feeding-stuffs for cattle, and as a rule in England, America, and Germany the seed-crusher has little interest in its disposal other than as cattle food.

The value of solvent-extracted cake for "compound" cattle foods is usually about £5-6 per ton, and is assessed mainly on the nitrogen content as an indication of the amount of proteins present. It is mixed with molasses, starchy materials, and sometimes other and inferior material as "filling," in order to produce what is known to the trade as "compound" cake.

"Straight" oil-cake, on the other hand, is valued primarily on the basis of the fatty oil left in it, and realizes as a rule about £10-12 per ton.

The procedure adopted in disposing of the products from the oil-extraction plant, either from the hydraulic press, or after removal of solvent by steaming in the solvent-extraction filter presses, consists mainly in trimming the

edges of the cakes to remove any imperfectly extracted portions, and passing them through an air-drying system in order both to remove moisture and to cool the cakes, which may then be packed whole, coarsely broken, or in the loose condition as extracted meal.

The composition of some typical oil-cakes is given as follows by Smetham and Dodd :

—	Water.	Oil.	Albuminoids (6·25 x %N).	Digestible carbo- hydrates.	Woody fibre.	Mineral ash.
Coconut Cake, English make ..	9·0	9·2	21·2	43·0	11·9	5·7
Copra Cake, Borneo ..	10·7	10·3	19·8	44·2	9·6	5·5
Palm Kernel Cake, pressed ..	11·1	7·4	17·1	48·4	11·9	4·1
Palm Kernel Cake, extracted ..	10·7	1·8	19·1	49·1	15·4	3·9
Cottonseed Cake, decorticated, American ..	7·9	8·7	46·5	25·4	6·3	5·3
Cottonseed Cake, decorticated, Indian ..	7·5	10·0	35·4	32·0	7·8	7·4
Cottonseed Cake, undecorticated, pressed ..	13·8	6·6	24·6	29·3	21·2	4·6
Cottonseed Cake, undecorticated, extracted ..	9·2	1·3	26·9	28·4	28·5	5·8
Linseed Cake, English pressed ..	11·2	9·5	29·5	35·5	9·1	5·2
Linseed Cake, English extracted ..	13·2	3·0	34·8	34·7	8·8	5·7
Soya Bean Cake, English, pressed ..	12·7	11·1	38·8	26·5	5·9	5·1
Soya Bean Cake, English, extracted ..	11·8	1·5	44·0	32·1	5·4	5·2
Groundnut Cake, undecorticated ..	8·6	11·6	26·0	26·2	19·3	8·3
Sunflower Seed Cake, Husked ..	7·8	10·0	37·0	21·1	16·5	7·6
Rape Seed Cake, Fresh ..	8·1	9·3	36·4	29·3	8·0	9·0
Rape Seed Cake, extracted ..	9·9	3·3	35·4	31·6	11·0	8·8

II. ANIMAL FATS

Rendering.—Whilst it will be found that hydraulic pressure or solvent extraction is also employed for extracting fat from animal sources in a few instances, the most usual principle is that known as "rendering," a term which originally signified the isolation of fat from animal tissue by the simple action of heat, which causes the cells to burst and the melted fat to run together in a form more or less convenient for collection.

Although the fundamental principle of cell rupture and exudation of liquid fat remains, the application of fat-

rendering in its modern forms is vastly different from the original crude manner in which the procedure was carried on. This will be evident when it is remembered that the enormous quantities of edible lard and edible tallow consumed annually are practically all prepared by this method in one or other of its present forms.

As the technical procedure is broadly similar, whether the animals consumed are pigs, cattle, sheep, whales or other marine mammals, or fish, it is convenient to discuss in one place the various modifications of the rendering process which are in common practice at the present time.

Preparation of the Organs or Flesh for Rendering.—The same principles apply here as in the case of vegetable fats, namely, removal of the fat-containing material from adjacent non-fatty matter (or from adjacent parts containing fat of a different quality), cleansing of the material and its comminution to a state adaptable to the extraction process.

The carcases are in general dissected by hand (preferably as soon as possible after death), and in cases where the animal is not to be rendered as a whole the organs or parts of the flesh containing the most valuable fat are separated from the rest of the body, whilst the intestines, bones, etc., are most frequently worked up separately from the main portions.

The separated portions are collected, scraped to remove adhering non-fatty tissue where necessary, and thoroughly washed in water, and are then passed to machines which chop and mince them to a sufficiently fine state of division for rendering. This varies from comparatively fine pieces of kidney fats from the pig or ox to fairly coarse lumps of material such as whale blubber or fish livers.

Rendering of Animal Fats for Edible Purposes (i) in the absence of Water.—The vessels employed for rendering edible fats are constructed of iron lined either with tin or enamel, usually the former. For operations below 100° C., they may consist of cylindrical or rectangular tanks of large capacity, fitted with closed and open steam coils, and

supplied with mechanical agitation and with a skimmer pipe for removal of liquid fat from the upper part of the charge when rendered ; except for a light lid to prevent access of dust, the vessels do not require to be closed.

The highest qualities of edible lard and some tallow are rendered in apparatus of this type by charging with selected parts of best fat, which has been cleaned and cut up into small pieces, and applying sufficient heat to raise the temperature of the whole to 40–50° C., the exact temperature being carefully regulated according to the particular material in process and agitation being applied.

The fat gradually escapes from the cell tissues and floats to the top, whilst the tissue, which still holds notable quantities of fat, sinks to the bottom.

Rendering of Animal Fats for Edible Purposes

(ii) in presence of Water:

(a) *In Open Digesters* (*i.e. below 100° C.*).—The residues from the preceding process, or fresh material, may also be rendered in apparatus similar to that described, by conducting the operation in presence of water in approximately equal amount to that of the fatty material. Heating is effected either by steam in the closed coils or by open admission of steam, and the process is carried out at the same temperature as above for the highest edible qualities, or at higher temperatures (up to the boiling-point of water) where a high yield of fat (of somewhat lower quality) is desired. The fat is skimmed off and the separated residues are usually submitted to further extraction by the autoclave process.

(b) *In Autoclaves* (*i.e. above 100° C.*).—In this process large tin-lined jacketed vessels ("digesters") provided with open steam coils and capable of working up to a pressure of about 150 lbs. per sq. in. are used. The fat charge, consisting either of fresh material, or residues from open rendering, is placed on a perforated false bottom in the autoclave with a small proportion of water and heated in presence of a current of open steam for several hours, usually at a pressure of from 60 to 90 lbs. per sq. in. In these cir-

cumstances practically the whole of the fat is dislodged from the tissue and is subsequently drawn off after the pressure has been released and the contents settled.

The quality of the fat obtained by this more intensive procedure is naturally not so high as that obtained by low-temperature rendering, since non-fatty organic matter is more liable to be separated and pass to some extent into solution in the fat, whilst some hydrolytic action may proceed so that the free acidity of the fat produced may be appreciable.

Rendering Animal Fats for other than Edible Purposes.—The procedure is much the same as in the foregoing cases, except that it is not customary to employ lined vessels and that the extraction is always performed in presence of water, which considerably accelerates the breaking down of the fat-cells.

The best qualities of fat are mainly obtained by primary rendering in open digesters, but very large quantities are produced by the autoclave or closed digester process.

It is now only necessary to recapitulate the chief grades of the more common animal fats which are rendered on a technical scale, together with the few instances in which solvent extraction is employed, since the various classes of these fats occurring in commerce have already been outlined in Section II., Chapter II. (pp. 137, 144, 147).

(a) *From Domestic Animals (Pigs, Cattle, Sheep).*—The whole of the fat of the pig is worked up for technical purposes in the forms indicated in the table on p. 214 :

(b) *From Marine Animals (Blubber).*—The chief oils extracted technically are those of the whale (including the sperm varieties), seal, and dolphin ; the fish oils in which the whole fish is worked up (sardine, herring, salmon, menhaden oils) are produced by similar methods to the blubber oils, except that extraction by hydraulic pressure is occasionally substituted for rendering with water in closed or open digesters (*cf.* Section II., Chapter II., pp. 140, 144).

The modern procedure of whale oil rendering, frequently carried out on board a specially fitted steamer or in factories

No.	Product.	Source.	Mode of extraction.	Application.
1	Neutral lard, No. 1 ..	Kidney and bowel	Rendering below 50° without or with water.	Edible lard.
2	Neutral lard, No. 2 ..	Back fat	Rendering in autoclaves	" "
3	Leaf lard ..	Residue from Nos. 1 and 2	Lowest quality of edible lard.
4	Prime steam lard ..	All parts, other than those in Nos. 1, 2, 7, and 8	In soft edible oils.
5	Lard oil ..	Neutral, leaf or steam lard	Cold pressing of the products Nos. 1-4.	Edible fats or high-grade lubricant.
6	Lard stearin ..	Skins and adjacent flesh	Rendering in autoclaves	Soap or lubricant.
7	Skin or yellow grease ..	Intestines and remainder of animal.	"	Lubricating grease.
8	Brown grease ..			

The utilization of cattle and sheep in tallow and fat production may be summarized similarly as follows:

No.	Product.	Source.	Mode of extraction.	Application.
1	Premier jus ..	Suet	Rendering below 50° C. without water.	Margarine, etc.
2	Oleo oil ..	From Premier jus	By pressure	Margarine, etc.
3	Oleostearin ..	All other parts of ox, except skin, bones, and intestines.	Rendering in autoclaves	(Margarine, soap, candles, etc.)
4	Rendered beef tallow ..	All parts of sheep, except skin, bones, and intestines.	"	Soap and candles, etc.
5	Rendered mutton tallow ..	From rendered tallow ..	By pressure	"
6	Lower grade oleo oil ..	Bones of sheep and oxen	Autoclave or solvent extraction.	{ Soaps, lubricant. } Soaps, candles
7	Lower grade oleostearin ..	Skins of sheep and oxen	Rendering in autoclaves	Lubricant and low-grade soaps.
8	Bone fat ..	Sheep's wool	Scouring (solvent extraction)	Soap or lubricant.
9	Skin greases ..	Feet of cattle	Rendering in autoclaves	Lanolin; waste product.
10	Wool fat ..			High-grade lubricant and leather dressing.
11	Neat's foot oil ..			

at the whaling fleet bases, was described on p. 144, the products being as follows :—

Product.	Source.	Mode of extraction.	Remarks.
No. 0 grade	Blubber ..	Boiled with water in open digesters.	First runnings of very high-grade oil.
No. 1 grade	"	" "	Oil from more prolonged boiling of the blubber.
No. 2 grade	Residue from Nos. 0-1 grade.	Rendered with water in autoclaves.	Yellow, up to 5 per cent. free acidity.
No. 3 grade	Flesh other than blubber.	" "	Brown, up to 10 per cent. free acidity.
No. 4 grade	Bones and offal	" "	Very low-grade oil, containing mucilage and protein.
Guano ..	Final residues from Nos. 2, 3, and 4 grades.		Utilizable as manure.

The total yield of Nos. 0 and 1 grade oils should reach 70–80 per cent. of the whole of the extracted oil.

(c) *From Fish Livers.*—The extraction of cod liver oil and the corresponding low grade cod oil has already been described on pp. 140, 143, from which it will be seen that the method adopted is rendering in presence of water with a current of steam in open digesters.

With the exception of the "neutral lards," leaf lard and premier jus, all the materials described in this section dealing with animal fat extraction require refining from suspended tissue, etc., before use as edible fat; whilst the qualities employed for non-edible purposes frequently require the removal both of suspended matter or bodies in colloidal solution and of traces of colouring matter by bleaching.

The procedure employed to effect these ends is discussed in the next chapter.

CHAPTER II.—THE REFINING OF FATS

Introductory.—It is probably more frequently the case than otherwise that fats as extracted are not in the most suitable condition for use as raw materials in subsequent processes. Thus nearly all edible fats are at the present time subjected to refining from various undesired substances which are usually present in the extracted fats, although in minute proportions, and many oils destined for use in soap-making (including glycerine recovery) are also refined to some extent, although many others, especially tallow and the nut oils, are often employed as extracted without further purification. Further, whilst the comparatively low-grade oils used, for example, in certain of the leather-dressing processes or as lubricants may not require purification, for the better qualities of leather or for special lubricants, and again for the paint industry, it is requisite to use oils which comply with certain specifications as to purity, and the problems of refining must be considered. Since the materials which require removal from the fat are the same in most of these cases, it is deemed advisable to deal with them collectively at this point and not in connection with the individual industries.

The impurities present in freshly prepared fats, whether expressed, solvent extracted, or “rendered,” may be grouped under the following heads :

- (i) Relatively coarse suspended matter, including mucilage (vegetable or animal tissue), albumenoid matter, resinous bodies ;
- (ii) Exceedingly fine suspensions of colloidally dispersed material of either of these types, which may even be present in an apparently transparent oil ;
- (iii) Natural colouring matters extracted from the vegetable or animal tissue and dissolved in the fat ;

(iv) Free fatty acids produced by hydrolysis from the natural fat ; and

(v) Semi-volatile compounds dissolved in the fat and conferring upon it an undesired characteristic odour or taste.

Broadly speaking, the refining processes in common use include :

I. *Coagulation* by settling the crude fat either at once or after heating it alone or more frequently with water or brine.

This removes all the coarse suspension and frequently also some part of the colloidally suspended matter, whilst it may also improve the colour and odour of the fat.

II. *Adsorption* by treatment with a siliceous earth or with charcoal.

This procedure in many cases almost completely removes from the fat both the colloidally dispersed impurities and the colouring matter present, whilst odoriferous compounds may also be adsorbed. Consequently it is one of the most important aids at the command of the fat-refiner.

III. *Chemical bleaching* by a variety of specific agents. Chemical processes are used to remove the coloured compounds present in certain cases, either by oxidation or reduction to a colourless derivative, or by more profound decomposition with a violent agent such as concentrated sulphuric acid.

IV. *Alkali Refining*.—The main object of a wide variety of processes involving the treatment of fats with alkalies is, of course, to remove free fatty acid and leave a neutral fat ; but considerable improvement in colour is also frequently effected, and thus alkali refining is not to be considered only as a means of obtaining neutral fat, but in conjunction with the question of bleaching.

V. *Passage of Steam or other Inert Gas through the Fat at High Temperature and Reduced Pressure*.—This is the principle employed in modern practice in order to remove the semi-volatile odoriferous impurities present in a fat, and to obtain a completely odourless and tasteless product ; but suggestions have also been made to utilize this principle

to distil away in addition the free fatty acids which are present, thus eliminating the necessity for alkali refining.

It is evident from the above outline that almost any of these methods of refining tends most frequently to remove one of the five classes of impurities fairly completely, whilst in addition a more or less complete removal of another class may also be effected at the same time. It is therefore most convenient to consider each of the five general principles of fat-refining in detail separately, the attention of the reader having now been directed to the nature of the purification effected in each case. The range of the various processes is also indicated by references in the text which will further emphasize their utility in specific cases.

Lewkowitsch has aptly pointed out that the refining of each individual oil or fat must be considered as a problem *sui generis*, that the technical procedure to be adopted must vary greatly with the nature of the individual fat and must be determined by experimental trial in each particular case in order to attain the best results.

I. COAGULATION METHODS

(a) **Simple Settling and Filtering.**—The crude extracted fat is placed in large tanks, if possible for several days, at such a temperature that it is freely liquid. Practically the whole of the relatively coarse mucilage settles fairly rapidly to the bottom of the tank where it coalesces to some extent, and clear oil is obtained either by drawing off the upper layers, or better by pressing the whole through the cloths of a filter-press.

This method is most frequently used in cases where the fat is of high quality, but is to be subsequently refined by alkali; the preliminary removal of suspended mucilage may lessen to a considerable degree the amount of neutral fat which is removed in an emulsified or "occluded" state with the fatty acid soap.

(b) **Settling after Boiling over Water or Brine.**—A very common practice is to heat the crude fat in large tanks (up to 100 tons capacity) by means of a current of

open steam, when the condensing steam exerts a coagulating action on the suspended matter and the latter is either drawn into the water layer or into a relatively small oil-water emulsion between the water and the fatty oil resting above it.

Frequently, also, the operation is conducted in presence of brine, solid salt being added at the commencement to the extent of 1 or 2 per cent. of the weight of fat treated.

In either case, the steamed fat is allowed to settle for a few hours and the lower layers of water (brine) and emulsion withdrawn. In modern plants the emulsion (or the whole of the aqueous layer, or of the steamed fat and water) is more usually fed continuously to centrifuges and the clear centrifuged oil separately collected. This, of course, results in less loss of oil as emulsion and usually, also, in the production of brighter and cleaner oils.

This procedure, like (a) above, is very frequently adopted with the more valuable edible fats such as the nut oils or groundnut oil prior to neutralization, and it is also extensively employed in the clarification of other oils such as palm oil, tallow, soya bean oil, whale oils and fish oils of good quality, etc.

(c) **Heat-treatment in the absence of Water.**—In a few instances clarification is promoted by heating the oil to a high temperature for some hours, when colloidally dispersed material separates out in the coagulated condition and falls to the bottom of the oil. This is notably the case with linseed oil, which is subjected to a temperature of 180–250° C. and thereby becomes paler and brighter, and also is found to absorb oxygen from the air more rapidly and consequently “dries” more readily.

Since, however, the oxidizing effect is also accelerated by the presence of substances which act as oxygen carriers and are known as “driers” (*cf.* Section VIII., p. 480), and which usually consist of small amounts of the fatty acid salts of oxides of manganese, cobalt, lead, etc., the operation is usually carried out in presence of a small amount of these oxides. The manufacture of “boiled”

linseed oil, as it is termed, therefore involves both the heat process of clarification and the combination of some of the fatty acids present with the metallic oxide "drier."

It has also been suggested to clarify oils by passing a current of dry (superheated) steam at a high temperature, a procedure which is more akin to simple heat treatment than to coagulating action induced by agitation with water ; this method, however, is rarely used in practice.

II. ADSORPTION METHODS

This group of refining processes is a very important one and extensively applied in the industry ; it depends on the property which a number of inorganic adsorbent materials possess of fixing either colloidally suspended matter or dissolved substances of relatively high molecular weight, such as the natural colouring matters. Consequently such processes are often efficacious both in clarification and in bleaching.

The amount of matter in fine suspension, or of coloured compounds, present in a fat is not very large ; it probably never exceeds 0·5 per cent. of the weight of fat and may be much less, whereas the adsorbents employed may be capable of combining with, say, 5 per cent. or more of their weight of these substances. An adsorption process is to a considerable degree a balanced action, so that to ensure practically complete removal of the foreign matter more adsorbent must be used than is actually adequate to combine with the latter, but in spite of this the proportion of adsorbent necessary in relation to the fat treated is, for the above reason, very small.

The actual percentage employed varies according to the specific nature of the crude fat and to the degree of bleaching which it is desired to effect, and should be determined for each case by laboratory trials. It is only possible to give sufficient illustrations of the manner in which refining by adsorption methods may be carried on to show the usual limits of temperature, concentration of adsorbent, etc., which are of general utility.

In fat-refining the method used is almost exclusively agitation of batches of fat with a small proportion of the adsorbent. In other industries, for example, petroleum refining, it is more often the practice to filter the oils through stationary beds of adsorbent material until the latter are exhausted and ready for recuperation. The filtration method is, however, less suitable for fats for a variety of reasons, notably the fine state of division and soft, clogging nature of most of the agents in common use (leading to difficulty in filtration) and the amount of fat left in contact with the adsorbent after draining (causing excessive loss of adherent fat, the latter being as a rule relatively costly even in the crude state as compared with, for example, a mineral oil).

The procedure adopted is therefore to treat batches of the fat in cylindrical vessels which may have a capacity of, say, from 5 to 25 tons of oil, and which are provided with closed steam coils for heating purposes and with a mechanical agitator usually consisting of paddles set on a vertical axis which is driven by gear-wheels at the top of the vessel.

Frequently the operation is conducted under a vacuum of about 1-5 inches of mercury and a certain amount of volatile or odoriferous impurities are simultaneously withdrawn from the fat, apart from the action of the adsorbent. Whilst, however, the odour of some crude oils, especially fish oils, is much improved by the added vacuum treatment, the latter is insufficient at the temperatures employed for adsorption-refining to effect a complete deodorization of the fat such as is necessary if it is to be used for edible purposes. At the same time, the use of reduced pressure, quite apart from deodorization, is to be recommended in all cases because access of air to the surface of the heated oil, leading to partial oxidation and consequent deterioration in colour, odour, and other properties, is thereby minimized.

The *temperature* at which the treatment is carried out depends on the particular circumstances—the nature of the crude oil, the adsorbent used, and the end to which the refined fat is to be put.

If the object in view is the clarifying or "brightening" either of a high-grade crude fat or of a similar fat which has already been neutralized with alkali, agitation with adsorbent at 80-100° C. for an hour or so is all that is required; and if the fat is to be used for edible purposes it is better, *ceteris paribus*, to carry out the operation at a temperature not higher than 100° C.

If the problem is the removal of colloidally dispersed matter from an oil of a lower grade, for example with a view to the suppression of catalyst poisons during subsequent hydrogenation (*cf.* the next chapter, p. 253), treatment at a temperature higher than 100° C. is usually desirable in order to produce the best results. Various temperatures up to 200° C. or higher have been recommended in such cases, but, bearing in mind the possibility of damaging the oil (especially if highly unsaturated) by over-exposure to high temperature, it will usually be found that maximum efficiency is attained at temperatures not greatly exceeding 150° C. The time required varies according to the quality of the crude fat and the temperature of treatment, and diminishes considerably as the latter is raised: thus some oils may require three or four hours at 120° C., and only one hour at 150° C., or less at a still higher temperature.

Finally, there are specific cases of oil-bleaching which demand a special range of temperature and in some cases a duration of time which exceeds those already stated; these include more particularly the tallow and relatively highly coloured oils such as soya bean, maize, and palm oils. The best working conditions should be ascertained in such cases by direct experiment on small samples of the actual oil which is to be treated in bulk.

Choice of Adsorbent.—The most useful adsorbents for fat-refining are undoubtedly (i) the various types of charcoal which are on the market and (ii) fuller's earth in its different natural and artificially treated forms.

A number of other refining agents have been proposed from time to time, amongst which may be mentioned

kieselguhr and silica gel ; but these are not in general so useful as the former materials. They undoubtedly possess clarifying and bleaching powers, and it has been claimed that certain types of silica gel are exceedingly powerful refining agents for fats ; but it does not yet appear that any material can compete on an economic basis with fuller's earth or charcoal.

Charcoals.—Ordinary bone charcoal or animal charcoal possesses considerable refining powers for many fats, but charcoal prepared by incineration of selected woods is in general superior for the purpose. Coconut charcoal and beechwood charcoal are among the best for fat-bleaching.

Specially prepared, very voluminous charcoals are available which are produced from vegetable sources by processes which have not been fully disclosed. Exposure at a high temperature ($800\text{--}900^{\circ}$) to a mixture of steam and air is probably the basis of most processes for activation of charcoals. Some of these are exceedingly active adsorbents, especially for fats such as the hard and soft vegetable oils which are refined and bleached for edible purposes ; it is usually necessary only to use 1 per cent. or less of these charcoals on the weight of fat treated.

With ordinary wood or animal charcoal the concentration necessary is higher and may range from 1 to 3 per cent. of the fat.

The price of the special charcoals is naturally considerably higher than that of ordinary wood charcoal, and this, together with the relative concentrations necessary, has to be taken into account in determining the most efficient procedure.

It is also possible in some cases, where charcoal is valued for a specific bleaching action, to use it in admixture with the cheaper fuller's earth, which is usually capable of effecting considerable clarification so far as suspended colloidal impurities are concerned.

Fuller's earth is a siliceous mineral, containing also combined ferric oxide and alumina, and occurs in more or less isolated beds usually in association with greensand or

gravel ; it is of a soft, almost greasy, nature and varies in refining power somewhat markedly according to its source.

Fuller's earth is obtained from deposits in several parts of this country, *e.g.* Surrey and Somerset, and from extensive beds in Florida, U.S.A. (known in commerce as " Floridin "). Some deposits of fuller's earth are of relatively poor efficiency in fat-refining, although they are frequently quite useful for petroleum-refining ; it is necessary to bear in mind that the adsorbents most applicable to fatty oils and to petroleum oils are as a rule not the same in each case.

There are also on the market certain other earths, such as " Japanese acid clay " and " Tonsil," which are mineral earths which have been " activated " by chemical treatment, and which possess bleaching powers of a much more intensive character than ordinary fuller's earth. The general procedure used to obtain activated fuller's earth is to boil the latter with dilute (about 10 per cent.) mineral acid for a few hours (3 or 4) in a vessel fitted with mechanical stirring. Hydrochloric acid is frequently preferred, but sulphuric acid is also used. The activated earth is filtered and washed free from the mineral acid liquor. It has also been proposed to activate a paste of the earth with dilute sulphuric acid by electrolysis. The activation process can be combined in one operation with bleaching by agitating about 4 parts of fuller's earth with 100 parts of oil, adding 0·1-0·2 parts of concentrated sulphuric acid, and then heating to about 120-130°, when rapid bleaching is effected. Activated earths, whilst of general use with fats, have found particular application in the removal of the natural red and yellow colouring matters of palm oil and in the bleaching of tallow for good class soaps.

The concentration of fuller's earth used in refining is usually greater than that of charcoal and may be, according to circumstances, from 2 to 5 per cent. of the fat treated.

Recovery of Oil from Adsorbent.—When the agitating process is complete and the fat sufficiently clarified or bleached, the charge is cooled down to such a temperature that exposure to air will not harm the fat and then passed

through a filter-press, the clear oil being collected. The adsorbent will retain up to its own weight of adherent fat, much of which can be recovered in fair quality by steaming out the press. The remainder of the adherent fat may be extracted from the adsorbent cake by solvent, the operation being carried out in the press if this is constructed for the purpose ; the solvent-extracted fat, which may amount to 30-50 per cent. of the weight of dry adsorbent, contains of course coloured impurities which have simultaneously been removed from the earth or charcoal, and is relatively low in quality.

As a general rule the residual earth or charcoal is not suitable for further use in fat-refining except after special and expensive recuperation, and it is usually more economical to reject it and employ fresh adsorbent on each charge of fat.

The uses of the adsorption process may be broadly classified as follows :

1. Clarification and bleaching of alkali-refined high-grade fats such as palm kernel, coconut, groundnut, cotton-seed, sunflower seed oils, etc.
2. Clarification of crude fats such as whale, fish, soya bean, linseed, etc., oils prior to other chemical treatment, especially hydrogenation.
3. Bleaching of tallows for candle- and soap-making, and of certain waxes for polishes.
4. Bleaching of coloured vegetable oils, especially soya bean, maize, groundnut, cottonseed and palm oils.

It is important to note that bleaching by adsorbent materials effects complete *removal* of the foreign matter from the fats, whereas chemical processes of oxidation or reduction merely change the character of the coloured compounds, which are in general still left in solution in the fats in an invisible form.

III. CHEMICAL BLEACHING

Chemical methods of bleaching are frequently efficacious, but are not suitable as a rule if the fat is to be used for edible purposes, because the flavour is slightly but definitely

affected. Care must be exercised in all cases, moreover, to conduct the operation so that the unsaturated constituents of the fat are not attacked, otherwise the value of the fat, especially for soapmaking, is liable to be depreciated. Chemical methods are, however, widely employed in practice and the chief processes employed will be briefly described.

Oxidation Methods.—Many of the colouring matters present in natural fats are converted into colourless derivatives by mild oxidation, and various methods have from time to time been employed to this end : they may be classified as follows :

(a) *Oxidation by means of Air.*—Beeswax and other waxes are frequently bleached by exposing them in thin layers to the more or less prolonged action of air and sunlight.

The red and yellow colouring matters present in palm oil also disappear as a result of similar treatment, but rancidity also sets in and this method is not suitable for technical application.

The use of ultra-violet rays (from a mercury lamp) has also been proposed in conjunction with air as a means of bleaching oils, but this method has not hitherto been widely taken up.

In many cases, especially with palm oil and tallow, it is possible to effect considerable bleaching by agitation with a current of air at 90-120° C. in enamelled, tinned, aluminium, or plain iron vessels ; but under these conditions unsaturated glycerides also tend to absorb oxygen at the ethylenic linkings, and the products suffer in colour and possess a slight unpleasant acrid odour unless great care is exercised in the control of the oxidation process.

The process of air-bleaching, nevertheless, appears to offer useful technical possibilities in many individual cases and seems to be worthy of more attention than it has hitherto received as a subject of technical research.

(b) *Oxidation by Ozone.*—The use of ozonized air for fat-bleaching should receive mention, although it is not as yet employed on any large scale in the fat industries.

(c) *Oxidation by Hydrogen Peroxide.*—Several Continental patents have recently been applied for in connection with the use of concentrated solutions of hydrogen peroxide.

It is claimed that agitation of many fats at about 60–80° C. with 1 or 2 per cent. of a 60 per cent. solution of peroxide, or with from 2 to 5 per cent. of a 30 per cent. ("100 volume") solution of the reagent, effects excellent bleaching without introducing any detrimental flavour. It should be noted that the production of hydrogen peroxide solutions more concentrated than about 30 per cent. is a costly, and apparently at present not an economically feasible, proposition on any large scale.

The bleaching action frequently proceeds more readily in an acid medium, and the presence of about 1 per cent. of concentrated sulphuric acid in the fats often assists the process considerably. It has also been proposed to carry out the process in acetic acid solution, but this is hardly suitable as a technical large scale procedure if it can reasonably be avoided.

The hydrogen peroxide process gives good results with whale and fish oils and with many vegetable oils such as linseed, rape, soya bean, palm, and other oils, but is less suitable for coconut oil, tallow, and some other fats. It is a method which, as yet, is in its infancy and it is not yet clear how far it will prove capable of development. Hydrogen peroxide, of course, always has the great merit that its decomposition products are solely water and oxygen, and there are no chemical by-products in the ordinary sense left for subsequent removal.

(d) *Oxidation by Dichromate and Acid.*—This process is fairly widely used in bleaching tallow, palm oil, and a few other vegetable oils. As regards palm oil it has the distinction of removing the colour without affecting the characteristic odour, which somewhat resembles that of violets and is appreciated rather than otherwise in soaps; whereas bleaching by adsorbent earths removes both odour and colour.

The chrome bleaching process is usually carried out in lead-lined iron vessels of about 10–20 tons capacity fitted

with a perforated lead steam coil and a similar coil for air agitation. The raw oil, which has previously been boiled over brine and settled, is run into the vessel and brought to 45–50° C. by the passage of open steam. The requisite amounts of sodium dichromate (in hot saturated aqueous solution) and of hydrochloric acid (sp. gr. 1·14) are then run in simultaneously and steam cut off, agitation being continued by means of air until bleaching is complete. Suitable amounts of reagents are 18 lbs. of dichromate and 12 lbs. of commercial acid per ton of fat present. When the bleaching is complete, as indicated by examination of a small withdrawn sample, the contents of the tank are well settled and the aqueous acid liquor drawn off. The bleached fat is then washed with water by steam agitation at about 60–70° C. for about a quarter of an hour, settled and re-washed at a somewhat higher temperature after removal of the first wash-liquors. Two washes usually suffice to remove all chromium salts from the bleached fat.

(e) *Oxidation by Hypochlorite.*—This process is also used to a considerable extent, especially for tallow. It is carried out very similarly to the chrome bleaching method, and in either instance the bleaching action is effected by the agency of the liberated chlorine. The operation is conducted at a somewhat lower temperature than is the chrome bleach, and the dichromate solution is replaced by one of bleaching powder, or sometimes of sodium hypochlorite.

Reduction Methods.—In certain instances it has been found that reducing agents, such as sodium hydrosulphite in its various commercial forms Blankite, Rongalite, etc., are capable of removing the colour from fats or from the soaps prepared from the latter. The procedure is carried out on similar lines to the chrome bleach process detailed above, the reagent consisting of a solution of about 1 per cent. of hydrosulphite compound on the fatty matter present. The method is not extensively applied and is more useful for soaps than for the fats themselves.

Reduction processes give less favourable results in general

than oxidation bleaches because the colourless reduction product is frequently liable to re-oxidation on exposure to air, so that the colour "reverts" to some extent; further, the fat or soap bleached by reduction is usually somewhat dull in appearance, even when satisfactorily decolorized.

Refining by Sulphuric Acid.—Some oils are much improved in colour after agitation with a small proportion of concentrated sulphuric acid at a temperature of about 40–50° C. Obviously, however, this procedure is unsuitable for edible fats owing to risk of introduction of a slightly charred flavour, and also for very unsaturated oils such as whale oil and fish oils, the more highly unsaturated components of which would be charred and resinified by the concentrated acid.

The method is used occasionally for linseed, rape, and a few similar oils, and consists in warming the oil to about 50° C. in a lead-lined vessel fitted with a stirring device, and then adding 1–2 per cent. of its weight of commercial oil of vitriol and continuing the agitation without further heating for about $\frac{1}{4}$ – $\frac{1}{2}$ hour. The oil is then settled and the lower layer of acid drawn off, after which it is washed two or three times with hot water to remove all mineral acid.

IV. ALKALI REFINING

The primary object of refining fats with alkali is, of course, to remove the free fatty acids which are present and leave a perfectly neutral fat, but in many cases, and especially if a caustic alkali is used as reagent, considerable improvement in colour accompanies the process owing either to combination of colouring matter with alkalies or to coloured impurities being adsorbed and carried away with the soap produced.

The exact method used therefore varies, as usual, with the particular fat in question: if the fat is already of good quality and definitely more valuable in the neutral state than as fatty acid, the object is to remove as little neutral fat as possible with the soap, whereas if the fat can be markedly increased in value by the decolorizing action of

the alkali, a process may be employed which produces maximum bleaching effect at the expense of a certain loss of neutral fat.

Neutral fats are essential in the edible fat industry and to a large extent in oils used in paints, as lubricants, and for illuminating purposes, whilst it is desirable, although not essential, to carry out catalytic hydrogenation of oils in the absence of free fatty acids, which are of the nature of mild catalyst "poisons."

Of numerous methods suggested from time to time to effect neutralization of the free fatty acids, it is only necessary to deal with the employment of sodium carbonate solutions, caustic soda solutions, and milk of lime, these being the only processes in general use.

The removal of free fatty acid by distillation from the neutral fat in a current of inert gas may be added to these, inasmuch as it offers a possibility of avoiding in certain cases the use of alkaline chemicals and the loss of neutral fat in the soap produced. This process is, however, more nearly related to that of heat deodorization and will be referred to again in connection with this subject (p. 238).

Neutralization Equipment.—The alkaline treatment is best carried out in a cylindrical vessel of from 5 to 25 tons capacity, the bottom of which is tapered conically in order to promote efficient separation of the neutral oil from the soap solutions when the latter are drawn off. A skimmer pipe is fitted at the top of the tank, by means of which the upper layers of liquid may be removed without disturbance of the contents of the lower part of the vessel. The neutralizing pan is also provided with an efficient mechanical agitator mounted on a vertical central shaft and with open and closed coils for steam, which can thus be either blown into the oil or used as an external heating medium in the closed coils.

The manipulative technique required in order to prevent the formation of undue amounts of emulsions and to secure the minimum loss of neutral fat with the oil is considerable, and is to be acquired rather by practice than by precept.

The process is controlled mainly by the amount of heat and agitation supplied, whilst the separation of neutral oil from the soap and oil emulsion, or "foots," can be assisted if necessary by the addition of small proportions of brine or solid salt.

The disposal of the "foots" finally produced is a not unimportant economic problem, which is discussed at the end of this section.

Neutralization by Sodium Carbonate.—This procedure is employed when possible partly in view of the relative cheapness of soda-ash as compared with caustic soda, and partly because it is usually possible to obtain a higher yield of neutral oil by use of this reagent than with caustic soda. Whilst caustic soda has in most cases a more pronounced decolorizing effect, therefore, neutralization with carbonate is employed in the cases of high quality crude fats where it is desired to preserve the highest yield possible of neutral fat, and for refining other oils in which the main object is removal of free fatty acid rather than maximum decolorization.

A quantity of soda-ash, about 1 per cent. in excess of that equivalent to the free fatty acids to be neutralized, is dissolved in the minimum amount of boiling water and placed in the neutralizing vessel. The oil, previously heated in another vessel to about 80° C., is pumped cautiously on to the carbonate solution with agitation, the rate of addition being governed by the volume of gas liberated during the neutralization.

Heat may be applied cautiously by open steam during addition of the oil and the whole subsequently brought to 100° C. by open steam, the agitation being continued for about 20–30 minutes. If towards the end of this period undue tendency to emulsification is evident, salt is cautiously added in small quantities until the emulsion breaks. Agitation is then stopped and the oil settled, when the clear neutral oil comes out on top and the "foots" settle in a thick heavy mass at the bottom. The neutral oil is run off by the skimmer pipe and the "foots" withdrawn at the bottom of the vessel,

or the latter may if desired be completely saponified *in situ* by the addition of caustic soda and re-boiling.

This method gives a clear oil with, however, somewhat greater loss of neutral oil in the "foots" than if the following plan is employed :

The method of treatment is as above, except that heat is applied exclusively by the closed coils and no open steam is used ; in consequence the amount of water present in the oil is lessened by evaporation instead of being increased by condensation of the open steam current. At the conclusion of the process the soap is relatively dry and rises to the top of the oil on settling in a thick cake. The clear neutral oil is withdrawn from the base of the vessel, leaving the "foots" on top, and since in this condition the latter hold less entangled neutral oil, the yield of neutral oil is increased.

This method is therefore to be preferred for crude oils of high quality which are definitely more valuable in the neutral state than as fatty acids (soap).

It should be noted that the percentage loss of oil with the soap tends to increase as the proportion of the latter is higher. For this reason, when dealing with oils of high free acidity, e.g. 25-30 per cent., it is desirable to neutralize in stages, removing not more than about five per cent. of free fatty acid at each neutralization. By this means the losses of neutral oil can to some extent be controlled, but it is not as a rule an economic proposition to produce neutral fat from a crude oil containing more than 25 per cent. free fatty acid ; the quality of the neutral fat from such oils is not likely to be very good in any case, as a high free acidity indicates extensive fermentative decomposition of the crude fat.

Neutralization by Caustic Soda.—The procedure employed is exactly as indicated for the carbonate process, except that in this case the caustic liquor is gradually run into the oil, and not the oil on to the reagent. The liquor employed may vary in strength from 20° Tw. to 100° Tw. (9 per cent. to 47 per cent. NaOH), but as a rule 60° Tw. liquor (28 per cent. NaOH) is used.

For simple neutralization an excess of about 0·5 per cent. of the alkali necessary to combine with the free fatty acid present is employed, but in cases where definite decolorization can be effected this excess may be economically increased up to, say, about 2 per cent., and a certain amount of neutral fat hydrolysed, with beneficial results to the colour of the finished neutral oil.

In some instances, also, the colouring matters present, especially if phenolic or oxy-ketonic in character, are more readily fixed by the more concentrated solutions of caustic alkali, and it is in these cases that 80° Tw. or 100° Tw. liquor may be advantageously employed. It is also possible to carry out the main neutralization with 60° Tw. liquor, and follow this with a further application of more concentrated alkali to aid decolorization.

The oils which are most benefited as regards colour by alkali treatment are cottonseed oil, dark vegetable oils of the soya bean, linseed or rape groups, and marine animal and fish oils ; the preliminary oxidation products of the highly unsaturated acids present in the latter are dark red compounds which are readily soluble in concentrated alkalies.

The loss of neutral oil in the "foots" from caustic-neutralized fats tends to be somewhat greater than when carbonate has been used, and it will be gathered that the caustic alkali method is mainly employed when colour-refining as well as neutralization is in view.

It has become the usual practice in efficient refineries to reduce the neutral fat content of alkali refined soap-stock by passing it through centrifugal separators which operate continuously. A quantity of fair-coloured neutral oil is thus recovered (although usually not so pale as the refined oil itself), whilst the fat content of the soap stock is reduced to 10-20 per cent., as compared with perhaps 40-70 per cent., according to circumstances, in the absence of centrifuging.

Continuous refining by Alkali.—About 1933 a process for continuous alkali refining was designed in the United States, and is becoming frequent practice in America and to some extent in this country. It has so far found use

mainly in the neutralization of vegetable fats which are liquid at the ordinary temperature.

The plant consists essentially of an automatic device for regulating the caustic liquor feed according to the flow of oil, a mechanical mixer for the oil and the caustic lye, and a tubular heater through which the emulsion of oil and lye is rapidly brought to about 90° , after which it is passed through high-speed centrifugal separators in which the oil is first separated from the soap stock, and thereafter washed with water and similarly centrifuged.

The time of contact of the oil with alkali is less than one minute in the mixer and less than five minutes in the heater, so that hydrolysis of neutral fat is minimized. The loss of neutral oil in the soap stock is stated to be reduced by about 30 per cent. as compared with the batch processes.

Neutralization by Lime.—The apparatus and procedure are similar to the foregoing methods, the reagent being a thick cream of slaked lime and water; an excess of lime up to 1 per cent. of that necessary to combine with the free acid is desirable. The calcium soaps are insoluble in water and lead to intensive emulsification, and it is preferable to conduct the operation in a closed pan, heated by closed steam coils only, and to remove the water present by evaporation under reduced pressure after neutralization has been completed. The calcium soap is then suspended in the oil in a fine granular condition, and can be best removed by filter-pressing the whole charge.

The use of the lime process has been claimed to produce clearer, paler oils than the other methods, although it is doubtful whether the decolorization effected is greater than by the use of caustic alkali; but the great merit of the lime process, which counterbalances the extra cost of evaporation and filtration incurred, is the high yield of neutral oil obtained.

Any of the above methods should in technical practice reduce the acidity of the neutralized fat to less than 0·2 per cent. (calculated as oleic acid).

Disposal of the Soap ("Foots") Produced.—An

economical outlet for the "foots" from the neutral oil is an important factor which requires considerable attention in technical practice and which depends on the particular fat in question, together with the facilities offered in the refinery concerned.

It is possible, in the first place, as already mentioned, to pass the "foots" through a continuous centrifugal machine in which further portions of the liquid neutral oil are removed from the soap, which may then contain 10 per cent. or less of neutral fat.

"Foots" from the alkali refining of nut oils for edible purposes are normally of sufficiently high quality to be utilized directly as a basis for toilet or at least for household soap. If the fat refinery is operated in conjunction with a soapery an outlet is thus available, but otherwise the "foots" are usually boiled in wooden vats with dilute sulphuric acid and the recovered fat, which contains from 50 to 80 per cent. of free fatty acids and is termed in commerce "acid oil" is sold to soap or candle makers.

Similarly, cottonseed oil is refined by alkali in large quantities in the United States in factories which may deal exclusively with the production of edible oil, and the "foots," known as *cottonseed soap stock*, are racked off into barrels or tank-waggons and sold as such to soap makers, who find the material quite suitable as a constituent of the fat-base for lower grade soaps. Cottonseed soap stock is not only used in America, but is, or was formerly, also exported in fairly large quantities to Europe.

The soap stock from the more liquid fats, such as linseed, rape, soya bean, or whale oils, is similarly used directly to some extent in the manufacture of soft soaps for the textile and similar industries, but this does not absorb the whole of the material available.

In some cases it is feasible to hydrogenate the acid oils obtained from such material and obtain a semi-solid fat of sufficiently good colour to be utilized in soap, whilst in the cases of cruder oils the acid oil is so dark in colour that it is of little use except for distillation.

In these cases the material passes to the fat-distiller, who heats it in a fire- or gas-heated pot-still (which is best maintained under vacuum), into the contents of which a current of superheated steam is injected. The fatty acids volatile under these conditions distil over at about 250–300° C. and are condensed and subsequently chilled and pressed, whereby there results on the one hand "oleine" (the fatty acids liquid at ordinary temperature) and "stearine" (the solid pressed residual acids). Such acids find a certain application in candle and soap manufacture, and in the leather trades (see Section VI., Chapter I., p. 413).

The still-residue consists of a dark solid pitch amounting to 10–13 per cent. of the original charge. The yield of distilled acids depends greatly on the nature and condition of the original acid oil; the more highly unsaturated acids undergo considerable pyrogenetic and profound decomposition at the temperature in the still, and naturally the proportion of the pitch is much greater when these are present in large amounts, as in linseed oil or whale oil.

It is also possible, and has been recommended, to esterify acid oils with glycerol (or alcohol) and thus to convert the bulk of the free fatty acids present into neutral esters. Fatty acids, when heated with excess of alcohol in presence of one or two per cent. of concentrated sulphuric acid, are readily converted into ethyl esters, and the small amounts of unchanged acid can be removed along with the mineral acid by alkali. Again, glycerol and fatty acids readily unite to form neutral glycerides when heated together at about 160–180° in a vacuum in presence of traces of naphthalene sulphonic acid or similar aromatic or hydroaromatic sulphonic acids. This procedure has been applied to some extent to the conversion of "acid oils" into neutral glycerides, but a certain degree of darkening is liable to accompany the esterification, and the products are not very suitable for use in edible fats. To obtain triglycerides, the fatty acids must be present in excess of the equivalent amount of glycerol used, and unchanged acids again removed by alkali from the esterified material. If glycerol is used in

excess of that necessary to form triglycerides with the acids present, di- and mono-glycerides will also occur in the final product.

Ethylene glycol can be used in place of glycerol as the esterifying alcohol, and a process has also been worked out for combination of ethylene oxide with fatty acids to yield di-esters of the glycol; but the fatty esters of ethylene glycol cannot be safely utilised in edible fats.

V. DEODORIZATION

Complete deodorization of fats is only necessary when these are intended for edible purposes, whereas the methods hitherto dealt with in this chapter are frequently applied when the fats are destined for a variety of other uses. Since, however, the process is essentially one of refining or purification, it seems preferable to refer to it here rather than in the section devoted to the edible fat industry.

The process is as a rule carried out after the free fatty acids have been removed and after any necessary bleaching action has been performed, and consists in heating the fat in closed iron or aluminium vessels to a temperature of about 160–220° C. by means of high-pressure steam in closed coils, the vessels being exhausted at the same time to the highest vacuum which can be maintained economically (usually 0·5–2 inches of mercury). Steam, superheated to about 200° C., or higher, is passed in a fine stream through a coil at the base of the oil charge.

The method thus consists in steam distillation at a very high temperature and under much reduced pressure and effects the removal of ethereal, hydrocarbon, or other substances present in small amounts in the fat and of comparatively high boiling point (say 150–180° C.). Such compounds frequently possess distinctive taste and smell, and must be completely removed before the fat is acceptable for edible use. Since it is necessary to remove the last traces of these bodies, the process is somewhat lengthy and may require twelve hours or more for completion, after which the charge is cooled down to below 100° C. under

vacuum and is then ready for use as a component of margarine, vegetable butter, etc. It is this process which unfortunately is bound to destroy any vitamins present in the original fat; but a low-temperature deodorization process, although it would be of extraordinary value, is not likely to be devised at all easily.

The actual working conditions used vary somewhat widely and are more or less secret; but obviously the process is effected more rapidly the higher the temperature, the limits to which are set by relative cost of heating and by the risk of damage to the fat above 180–200° C. Similarly, the higher the vacuum the more rapid and complete will be the deodorization, but again the limiting principle is the economic factor, the cost of reduced pressure mounting rapidly after the vacuum to be attained reaches a certain point. In recent years, however, the vacua attained technically have been much improved, with corresponding decreases in the time of exposure of the fat to the high temperature involved, and consequent improvement in the colour and quality of the deodorized products.

Suggestions have been made to conduct the deodorization in a continuous apparatus so that the fat is exposed to the high temperature only for a short time and in relatively small quantities at any one time.

Simultaneous Deodorization and Removal of Free Fatty Acid.—The last-mentioned system of continuous deodorization has been adapted so as to form the basis of processes for concurrent deacidification and deodorization of fats, or for their deacidification only.

Suggestions on these lines appear in patents by Craig and Lever Brothers, Ltd., who proposed to pass an intimate mixture of oil and fuller's earth through a series of horizontal tubes, heated at 250–300° and under a high vacuum, in counter current with a stream of superheated steam.

The advent of processes of this kind in large scale practice has followed the advances in production and maintenance of higher vacua in technical plants. Much

greater efficiency is naturally obtainable at pressures below 10 mm. or 5 mm. of mercury than at 25–30 mm.

A somewhat new principle was introduced by Wecker, who took advantage of the violent expansion produced in a high vacuum by the injection of droplets of moisture (wet steam) into fats or fatty acids at a high temperature, with consequent volatilization of the free acids. The fatty material is passed in thin horizontal layers through a reaction vessel heated to 240–270°, in a vacuum of 5–10 mm., where it meets a current of wet steam distributed through atomizing jets. The vapours pass to condensers where the fatty acids are separated, whilst the deacidified and deodorized oil passes to a cooler. The process, especially in regard to the technical production and maintenance of the highest possible vacuum, was modified and further developed by Lurgi. A number of large scale plants based on the Wecker and Lurgi designs are now in operation.

The processes were originally intended to eliminate the need for alkali refining, and in the case of nut oils (with their high proportions of lauric and lower acids) the free acidity can no doubt be reduced to a sufficiently low figure. It appears to be the general experience, however, that in the more usual type of fats, in which oleic and acids of similar molecular weight contribute the bulk of the free acidity, it is not usually possible to reduce the free fatty acids in the product to below 0·5–1·0 per cent. Consequently, although these processes are very useful in reducing the free acidity of crude fats containing 10 per cent. or more of free fatty acid to the amount mentioned, it is generally necessary to complete the removal of the latter by alkali refining.

The Wecker and Lurgi techniques seem, in fact, to have proved more useful in the deacidification of crude fats than in the original intention of combining deacidification, bleaching and deodorization in one operation. They also represent the most efficient form of still for the technical distillation of fatty acids from hydrolysed fats (see this Section, Chapter IV., p. 279, and Section VI., Chapter I.,

p. 413); it has been stated that a crude split fat containing 95 per cent. of fatty acid will yield 94 per cent. of pure, pale fatty acids by this process, given maintenance of a vacuum of 3-5 mm. and minimum time of exposure of the fatty acids to the distillation temperature.

Another form of continuous deacidification process has been proposed by Stiepel, who preheats the crude oil and then passes it in a thin film through the "distillation zone." In this zone the oil film itself is not directly heated, but receives radiant heat from a directly heated surface parallel and close to the oil film. The intervening space is held under high vacuum, but a current of inert gas passes through it which carries away the free fatty acids and other volatile matter. This process has probably not yet come into technical use; it is intermediate in principle between the Wecker plants and the "molecular still" to which some reference must finally be made.

The "molecular still" involves the evaporation of molecules from a liquid surface and their condensation on a cooled surface close to the heated liquid film. It is evaporation rather than distillation and takes place at extremely low pressures (0.0001 mm. and below) and at accessible temperatures (100-250°) in the case of fatty acids and glycerides of the usual molecular weight. By passage of a crude oil through such a still, therefore, it is possible to separate from it (i) non-fatty matter of lower molecular weight than the free fatty acids; (ii) free fatty acids, and (iii) the glycerides themselves, leaving a residue of non-fatty or polymerized or oxidized fatty compounds.

This technique has already found some application in the evaporative distillation of concentrates of vitamin A and similar compounds from oils relatively rich in these constituents. The cost of the plant, and of the extremely high vacuum necessary, would appear to render unlikely its use in the large scale deacidification of fatty oils, but the method should find mention in the present survey of possible technical means of removing fatty acids from oils by volatilization.

CHAPTER III.—FAT-HYDROGENATION

Historical and Theoretical.—The fats which are liquid at ordinary temperature preponderate in nature over those which are solid, whereas the demand for solid fats of various kinds for candles, soaps, and edible purposes is on the whole greater than that for the liquid fatty oils ; so that the solid fats tend normally to be more valuable than the liquid oils. Numerous attempts were therefore made to convert the unsaturated glycerides into the higher-melting saturated compounds on a technical scale, such as heating oleic acid with phosphorus and iodine, or fusing it with caustic potash and producing palmitic acid (Radisson), or converting it into hydroxystearic acid and stearolactone by heating with zinc chloride (Benedikt) or sulphuric acid (Geitel) ; none of these processes (except Radisson's) proved successful in practice.

In the meantime Sabatier and his co-workers showed (1897–1905) that many ethylenic organic compounds combined with hydrogen and formed the corresponding saturated derivatives when exposed in the state of vapour to the action of certain reduced metals, especially nickel. Sabatier, however, noticed that condensation of a film of liquid on the metal used suppressed all action, and concluded that the process only took place in the gaseous state. He found, as a matter of fact, that oleic acid vapour was thus converted to stearic acid, but the technical operation of the hydrogenation of oleic acid vapour was obviously enormously difficult, whilst that of the non-volatile glycerides was evidently impossible.

However, in 1902 it was stated by Normann that liquid fats and fatty acids could also be hydrogenated as such in presence of nickel, copper, platinum, or palladium, and in

the course of a few years the technical details of the process were fully worked out, and since about 1911 enormous quantities of liquid fats have been transformed into the more valuable solid fats by hydrogenation in the liquid state.

At the time of the work of Sabatier and of Normann, the fundamental theory underlying the subject of catalytic action (of which fat-hydrogenation is a particular case) was very imperfectly developed, but much research has since been devoted to this subject, which is of vital technical importance not only in the fat industry, but in the modern manufacture of ammonia, nitric acid, sulphuric acid, and many other important materials. It is not possible here to go fully into the development of the theoretical side of the subject, but a statement of the views at present accepted must serve as a standpoint from which it should become relatively easy to understand the technique adopted in fat-hydrogenation.

It is obvious, surveying catalytic action as a whole, that specific substances are necessary to effect specific changes—the kind of material which is catalytic for a given process is restricted, and what is effective in promoting one type of chemical change may be quite inert as regards another.

Further, so far as hydrogenation is concerned, it has become quite evident that the organic compound is definitely associated with the metal catalyst during the process, just as is the hydrogen. Taylor and his co-workers, amongst others, have shown quite conclusively that substances which interact in presence of a third (catalytic) agent are individually adsorbed at the surface of the latter prior to actual chemical action, and that the heats of adsorption are of the order of a mild chemical action when active catalysts are employed as adsorbents. Armstrong and Hilditch deduced from kinetic measurements and other considerations that an "intermediate complex" is formed between the catalytic metal and unsaturated organic compound, as well as between the former and hydrogen. In common with several other investigators, they also emphasized the selective nature of hydrogenation: fre-

quently, of two or more ethylenic linkages, one is attacked preferentially to the rest, which remain unaltered until the preferred position has been saturated, in spite of ordinary considerations due to the operation of the law of mass action.

Contemplation of these facts and of others which cannot be detailed here but which lead to similar conclusions, has led to the replacement of earlier theories of catalysis at solid surfaces by conceptions somewhat as follow. The surface of a catalytically active body will not be smooth, but will contain local excrescences in which some of the atoms are partially extruded from the main boundary surface of the crystal and in consequence have some of their affinity free and not satisfied by linkage with adjacent atoms within the crystal lattice (Taylor). Such specially active areas may be due to specific fields of force caused by special configurations of the atoms in these parts of the catalyst surface (Constable) rather than by the presence of atoms partially extruded from the surface. Schwab and co-workers have produced evidence that the "active points" are concentrated along phase boundaries, which may be the crystal edges of the micro-crystals in the surface layer of the catalyst mass. All these variants of the general theory conform with the principles, now generally accepted, that catalytic chemical change at a solid surface is preceded by interaction ("activated adsorption" or "chemisorption") involving forces of a chemical nature between the catalyst and each of the molecules entering into the action (in fat-hydrogenation, both hydrogen and the unsaturated fatty acyl groups); and that the solid catalyst must be regarded, not in the mass, but with respect to certain select atoms in the mass in which all the activity displayed is now believed to reside. In Taylor's words, "this picture supplies a reason for much of the mystery with which the subject of contact catalysis has been surrounded hitherto. For it shows that the properties of the contact agent are to be differentiated from the bulk properties of the substance of which the catalyst is composed; that it is rather the properties of the

individual atoms or molecules of the catalyst, with the changes in these properties induced by position and arrangement in the catalyst particle, which are of importance in catalytic change." It follows, therefore, that the worker on heterogeneous catalysis is in the somewhat unusual position of observing the behaviour of a selected few of the atoms or molecules present in the material under investigation, instead of dealing with the average behaviour of the whole assemblage of an enormous number of ultimate particles.

The present views permit us to understand why, although adsorption always accompanies (or rather precedes) catalytic change, all adsorbents are not necessarily catalysts, and why the same chemical substance may sometimes, and sometimes not, have catalytic properties. They also help to emphasize the essential conditions of suitable surface which must obtain before any catalysis occurs: when a suitable surface is present, no catalytic action will occur unless on that surface (whether deposited or forming the total surface *per se*) there is a specific chemical adapted to form appropriate intermediate complexes with all the interactants (e.g. if hydrogen and ethylene are presented to such a surface no formation of ethane will occur unless there is present some specific material such as palladium, platinum, nickel, or copper).

The more practical implications of the above views as regards fat-hydrogenation must now be dealt with briefly.

A surface of the type depicted will presumably tend (and has indeed been experimentally proved) to be affected by exposure to more than a definite degree of temperature: the action of heat, beyond a certain point, tends to reduce the number of atoms of maximum freedom and to produce a more even surface structure—a process analogous to "sintering" but occurring far below the actual melting point of the solid and having, indeed, no connection with any process of liquefaction.

Furthermore, any substance which is adsorbed by the solid atoms in preference to the interactants will thereby

diminish the amount of catalytic change, and it is especially to be noted that the atoms which are the centres of catalytic action will in virtue of their position be the first to come in contact with such preferred materials when present. This explains the formerly mysterious phenomenon of catalyst poisoning, and shows that a minute amount of impurity, insufficient to cover the whole surface, may suffice to suppress the normal functions of the catalytically active minority. It also indicates how it comes about that actual chemical transformation of the catalyst is not essential to, although it may accompany, toxic action ; and how, on the other hand, certain poisons, such as carbon monoxide, induce an apparent temporary paralysis of the catalyst which disappears when the poison is removed.

Finally, it is plain that an efficient catalyst must be so prepared and employed as to produce and maintain in being a maximum number of active atoms, and that, in combining a liquid with a gas, every opportunity must be afforded for maximum contact of the gas and the liquid with the active atoms in the solid surface.

These considerations are the guiding principles to be observed in the hydrogenation of fats, and the precautions necessary in carrying out the process are all based thereon.

In order to secure adequate contact of gas, liquid and solid, three independent methods are used in practice :

(i) *The agitation process* (Normann), in which mechanical agitation is used to produce an intimate mixing of nickel, fatty oil, and hydrogen ;

(ii) *The injection or circulation process* (Testrup, Wilbuschewitsch), in which the mixture of oil and catalyst is withdrawn from the lower part of the reaction chamber and injected as a fine spray into the gas-space at the top of the chamber by means of a circulatory pump ;

(iii) *The continuous process* (Bolton and Lush), in which a special stationary catalyst is employed and the oil passes downwards over it and meets an upward current of hydrogen.

Whatever the system employed, it will be realized that fat-hydrogenation is a somewhat complex industry and

includes, in addition to the actual hardening process, the problems of catalyst manufacture, hydrogen production, and preliminary refining of the fatty oils from catalyst poisons.

Production of Catalyst.—The method used depends on the system of hydrogenation employed, since fine particles of solid are most appropriate in the agitation and injection processes, whereas activated metal turnings are used in the continuous process.

The metal employed is almost exclusively nickel : palladium and platinum mounted in about 1 per cent. concentration on supports, such as magnesia, were formerly recommended partly on the score of relative activity and partly because it was held that they could be operated at a lower temperature than nickel. Any greater activity which they may possess as compared with nickel is, however, insufficient to balance the much greater cost of the metals, whilst the working temperature for nickel catalysts can, if necessary, be reduced to much the same degree as that of the noble metals, of course with proportionate diminution in the rate of hydrogenation. Cobalt and copper also display certain hydrogenating activity, but are not so widely applicable as nickel.

From the theoretical considerations already given it is easy to comprehend why smooth metallic surfaces, *e.g.* metal turnings or electrolytically deposited films, have no catalytic activity ; and it is of interest to note that nickel turnings can be made to display a certain activity by sufficiently intense mechanical abrasion until a state of powder is reached (Richardson).

The highest activity is, however, displayed by nickel which has been prepared by controlled reduction of its oxides, carbonate, or formate. It will be readily understood that completely reduced nickel so prepared is more liable to undergo loss of activity by a process analogous to "sintering" when exposed to increased temperatures than an incompletely reduced nickel oxide, or nickel deposited on a substratum of irreducible oxides : in the latter cases the interposition of oxide molecules may be supposed to

restrain the cohesive forces or affinities mutually exerted by adjacent atoms of the metal itself.

As a matter of fact, Sabatier, Kelber, and others have pointed out that completely reduced non-supported nickel cannot be exposed to a temperature much above 300° C. without loss of activity, whereas certain supported nickel catalysts will withstand a temperature of 500° C.

Whilst, therefore, in certain cases it may be desirable to employ non-supported nickel, it is often convenient to employ nickel mounted on a suitable support. This not only increases the power of resistance to high temperatures, but also has the advantages of giving a material which is much more readily filtered and which can be thoroughly washed with much greater ease prior to reduction. This washing is of considerable importance, especially if the catalyst is prepared originally from nickel sulphate, since no sulphur compounds must be present in the final reduced catalyst for obvious reasons.

Various materials have been suggested as supports for the nickel, including powdered pumice, powdered asbestos, powdered porous fire-brick, kieselguhr, china clay, dried silica gels, and numerous varieties of charcoal. The most commonly employed support is undoubtedly kieselguhr, whilst charcoal is used to some extent; the remainder of the numerous supports which have been put forward have probably not progressed, except in a few special cases, beyond the stage of insertion in a patent specification.

The preparation of a nickel catalyst on a powdered inert carrier may be outlined as follows:

The support is placed in a solution (about 10-20 per cent. concentration) of sufficient nickel sulphate to give a percentage of 15-30 per cent. of nickel in the finished catalyst, and the solution is brought to the boiling point whilst stirring is applied. A slight excess of sodium carbonate is added, either in the dry state or in concentrated solution, and the boiling continued for about 20-30 minutes. The contents of the vessel are then filtered and the residual cake thoroughly washed with hot water until all soluble

salts are removed, after which it is dried and reduced at temperatures varying from 300° to 500° C. according to the support used.

The reduced catalyst should be collected beneath a portion of the fatty oil to be hydrogenated whilst still in an atmosphere of inert gas, since it cannot be handled conveniently in bulk in the dry state without risk of sufficient exposure to atmospheric oxygen to affect its activity to a considerable extent. (For laboratory purposes small quantities of reduced catalyst can readily be stored in the dry reduced state without risk of deterioration, if the material is only transferred when quite cold and is stored in an atmosphere of inert gas, preferably (owing to its relative density) carbon dioxide.)

It may be stated that the only reliable guide to the efficiency of a preparation of reduced nickel is a small-scale comparative test of its power to effect the hydrogenation of an unsaturated compound of known composition, *e.g.* a fatty oil of suitably constant composition : the proportion of metallic nickel present, the density or colour of the product, etc., are not conclusive indications of the presence or absence of catalytic power.

To avoid handling reduced nickel catalyst in bulk, the reduction at about 250° of suitable nickel salts beneath the oil which is to be hydrogenated is now frequently adopted in fat hardening plants. Bedford and Williams recommended the reduction of nickel oxides in this way in 1910, and Wimmer and Higgins that of nickel formate in 1911. In recent years the use of nickel formate as the source of catalyst in technical fat hydrogenation practice has come into greater prominence. The simplicity of the reduction process counterbalances, to some extent, the greater cost of the formate, a quantity of which is suspended in some of the oil which is to be hardened and reduced therein by passage of a current of hydrogen through the stirred oil at 240°. When reduction is complete the oil with its charge of reduced nickel is cooled and mixed off with more of the oil to be hardened, the latter process being carried out at or

below 180°. The concentration of nickel in the oil during the actual hardening need not exceed about 0·2 per cent., and it can subsequently be removed by filtration through a bed of kieselguhr and, if desired, recovered by solution in acid.

Although not at present used on the large scale, reference should also be made to a type of nickel catalyst which possesses considerable activity, for hydrogenations in the liquid phase, below 100° and even at room temperature. This material, known as "Raney nickel catalyst," is prepared by the action of dilute sodium hydroxide solution on nickel-aluminium or nickel-silicon alloys, the excess of alkali being removed by washing, first with water, and finally with alcohol, beneath which the very finely-divided almost colloidal preparation of nickel is stored. Its activity is stated to be considerably accelerated by addition of a trace of platinum chloride to the hydrogenation system. It has come into considerable prominence of late for laboratory investigations. It is conveniently prepared for laboratory purposes, from alloys of nickel with about 50 per cent. of silicon or of aluminium, according to the directions given by Covert and Adkins, or according to the modified procedure advised by R. Paul.

Production and Purification of Hydrogen.—The amount of hydrogen fixed by different fats varies of course with their original degree of unsaturation, and with the extent to which they are hydrogenated : for example, the conversion of linseed oil into hard tallow suitable for candles would involve a reduction of about 150 in iodine value, whereas that of cottonseed oil into soft oil for soap might only necessitate a reduction of 25–30 in iodine value. On the average it is found that the weight of hydrogen absorbed over the ordinary range of oils treated in a fat-hardening installation is about 1 per cent. of the weight of fatty oil, or about 4,000 cubic feet of hydrogen per ton of oil treated. Since it is not usually economical to run a hydrogenation plant on an output of less than 200 tons per week of hydrogenated oil, the weekly consumption of

hydrogen is of the order of 800,000 cubic feet as a minimum, and may be four or five times this figure.

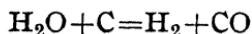
Thus the problem of hydrogen production is an industry in itself and should receive, in due perspective, much more space than can here be given to it. There are a number of excellent modern treatises dealing with the subject, however, to which some references are given in the bibliography on p. 281.

The hydrogen is produced from water, either by electrolysis or by the intermediate agency of water-gas produced by passage of steam over heated coke.

By far the best hydrogen for catalytic purposes is that prepared by electrolysis of water, but the cost of production by this means in the absence of cheap (water-power) electricity renders its employment almost out of the question in most English centres of the fat industry. The great advantage of electrolytic hydrogen is of course its freedom from traces of sulphur compounds and carbon monoxide; these are liable to be present in hydrogen from water-gas and affect the rate of hydrogenation in a pronounced degree.

The production of hydrogen from water-gas is effected by several distinct systems, and here it must be pointed out that the question of water-gas itself is an undertaking of no small magnitude which has also to be faced by the fat-hydrogenating operator.

Water-gas plants are nowadays a standard product of several firms of gas engineers, who install them according to their own designs: the chemical process concerned is given in the ideal equation



and the average composition of water-gas produced for hydrogen manufacture is of the order:

	Per cent.
Hydrogen	45
Carbon monoxide	40
Carbon dioxide	5
Nitrogen	5
Methane and other gases	5

Hydrogen may be separated from water-gas by liquefac-

tion of the carbon monoxide and dioxide, etc., present, and it has been technically produced by this means for fat-hydrogenation. The hydrogen so produced, however, is by no means free from carbon monoxide.

Another process which has been very widely used in England and in Germany consists in the alternate reduction of iron oxide ore by water-gas and passage of steam over the reduced iron, which regenerates iron oxide and sets free hydrogen. In one form of this process, with which the Lane patents were associated, the iron oxide, usually small fragments of hydrated spathic iron ore or similar mineral, is packed into retorts about 8 inches in diameter and about 9 feet in length, a number of these retorts being set horizontally in a brickwork furnace and heated by water-gas firing. The cycle of operations of the plant consists in reducing the ore by preheated water-gas for about 20 minutes, followed by a period of about 10 minutes when superheated steam is passed over the reduced ore. The spent water-gas from the reducing period passes to the heating flues and thence to waste, whilst the first portions of steam and hydrogen from the making period are also rejected in order to eliminate carbon monoxide as completely as possible. The hydrogen produced is passed to a gas-holder after purification as described below. At its best this process should yield one volume of hydrogen for not more than two volumes of water-gas consumed in reducing the ore and supplying heat.

A modification of this process devised by Messerschmitt and others has been much employed in Germany, and was adopted by the German authorities as the most efficient mode of producing hydrogen for airships. The retort batteries of the Lane system are replaced by a single vertical furnace of a kiln-like type ("Schachtofen"), which consists of a shaft of annular cross-section containing a large quantity of the broken iron ore with an internal heating flue in the centre and other flues surrounding the shaft externally. The whole furnace is enclosed in firebrick. The cycle of operations is much the same as in the Lane process.

Hydrogen prepared by the Lane, Messerschmitt, or Bamag methods will contain slight traces of sulphur compounds and about 0·2 per cent. at most of carbon monoxide.

The most efficient method of manufacture of hydrogen from water-gas, so far as consumption of water-gas and general costs are concerned, is the catalytic process patented by the Badische Anilin and Soda Fabrik and Bosch, which depends on the reaction



This change, known to physical chemists as the "water-gas equilibrium," proceeds at reasonable rates only in presence of certain metals or their oxides, and here again iron oxide is the ore found most suitable in practice. The process consists for all practical purposes in the continual reduction of iron oxide by the carbon monoxide and oxidation of the reduced iron by steam which has been added to the water-gas, thus converting the intermittent Lane or Messerschmitt method into a continuous or catalytic action. The hydrogen produced, after removal of carbon dioxide by scrubbing through water under pressure, will contain, in addition to small amounts of carbon dioxide and nitrogen, about 1·2 per cent. of carbon monoxide, which renders it less useful than Lane-Messerschmitt hydrogen for direct application in fat-hydrogenation. On the other hand, the efficiency of the process is such that only about 1·2 volumes of water-gas are required in practice to furnish 1 volume of hydrogen.

To render hydrogen produced industrially from water-gas suitable for use in fat hardening, it is necessary to purify it as thoroughly as possible from sulphur compounds and carbon monoxide.

Sulphur compounds may be removed by passage of the gas through hydrated iron oxide as in the case of water-gas, followed by similar passage over slaked lime or by scrubbing through a solution of caustic soda.

The carbon monoxide is more difficult to eliminate, and if not present to the extent of more than 0·1–0·2 per cent.

it may not be economical to remove it. It may be removed, as in the Badische process, by passage under compression through a scrubber containing an ammoniacal solution of a copper salt, or, in the case of small proportions, by adding about 1 per cent. of oxygen and passing the mixed gases over substances such as oxides of iron, copper, or manganese at about 100–150° C. Under the latter conditions the carbon monoxide is oxidized to some extent preferentially to the hydrogen, so that, although a small amount of hydrogen is also lost as water, the whole of the carbon monoxide is converted into carbon dioxide, which is not toxic to catalytic nickel.

Purification of the Fatty Oils prior to Hydrogenation.—The impurities likely to be present in fats which are to be hydrogenated are, in decreasing order of their toxicity to nickel, organic sulphur compounds, oxidized unsaturated fatty compounds (and fatty acids of low molecular weight), colloidal suspensions of mucilage, protein, etc., moisture and free higher fatty acids.

Free fatty acids, if the proportion does not exceed about 3 per cent. of the fat and if the acids are the saturated or unsaturated higher fatty acids present as glyceride in the natural fat, do not hinder the course of hydrogenation to an uneconomic extent, and oils of this degree of acidity may be quite readily treated without neutralization.

Moisture is to be avoided as far as ordinary precautions may be taken, because the catalyst, especially if supported on materials which are good adsorbents for water, tends to adsorb moisture preferentially to fat and may retain an adsorbed film of water, even at the temperature of reaction, thus tending to hinder unrestrained contact between liquid fat and the catalytic metal. It is not necessary, however, to attempt to maintain a rigidly anhydrous condition.

The other impurities mentioned are toxic even in small concentration, owing to their adsorption by the nickel in preference to that of the fatty compounds at the centres of unsaturation of the latter, and it is well to eliminate them as completely as possible.

Organic sulphur compounds are found but rarely in natural fats, although sulphur may be present owing to the oil having been extracted by carbon disulphide ; it is not usually necessary, however, to employ oils extracted by this solvent for hardening. Adequate removal of organic sulphur compounds is a somewhat difficult operation in technical practice.

Oxidized oils and traces of colloidal mucilage are removable by refining with caustic alkali and by adsorption with fuller's earth, etc., as described in the previous chapter.

The procedure to be recommended, therefore, is broadly as follows :

(i) To obtain maximum efficiency in hydrogenation, or when the fat will in any case have to be subjected to the refining processes concerned, it is preferable to neutralize the free fatty acid by alkali, and then treat the washed neutral oil with fuller's earth or charcoal at a temperature sufficiently high to remove the moisture present at the same time ;

(ii) A less costly method, applicable to crude oils of reasonable freshness and low free acidity, is simply to agitate them with a small proportion of adsorbent material at about 120–150° C. for a short time in order to effect removal of moisture and suspended matter ;

(iii) It sometimes happens that a raw oil is of sufficiently high quality to be hydrogenated efficiently without any preliminary treatment.

Apparatus Employed and Procedure in the Actual Hydrogenation.—It is necessary to consider separately the methods in which the oil is hardened in batches (agitator and circulating systems) and that in which the oil is hardened continuously (Bolton and Lush).

Agitation System.—The oil is conveniently treated in units dealing with up to 10 or even 20 tons at a time ; the vessels are usually cylindrical in section and heat is supplied either by an external jacket or, better, by an internal closed coil capable of taking steam up to 250 lbs. per sq. in. pressure. The agitation must obviously be as thorough as

possible in order to provide rapid renewal of the liquid films at the surface of the solid particles and to keep the latter evenly distributed throughout the body of the liquid. It is effected either by a vertical rotating shaft carrying one or several horizontal blades (the agitation being increased if intervening baffle plates are fixed on the sides of the vessel), by an inverted cone stirrer, or by a "Typhoon" type of stirrer or other suitable arrangement. Hydrogen is admitted at the base of the vessel and leaves by an exit pipe with safety valve leading from the top.

In operation, a charge of oil and catalyst is made up and pumped into the vessel; the concentration of metallic nickel may vary according to circumstances from about 0.1 to 1 per cent. of the fat. Hydrogen is admitted to eliminate any air from the vessel, agitation commenced, and heat applied by steam until the working temperature, which may vary between 120° and 200° C., is approached. A certain pressure of hydrogen is maintained in the vessel, usually from 2 to about 5 atmospheres; the action proceeds more rapidly if a certain amount of hydrogen is allowed to escape, and this unused gas may be collected and mixed with fresh hydrogen in further hydrogenations. The absorption of hydrogen proceeds more rapidly the higher the temperature, but the optimum rate of hydrogenation of fats is about 170–180° C., and above 200° C. there is some risk of development of undue colour and slight "burning" of the fat. It should be noted that, apart from this, fat-hydrogenation is usually accompanied by a bleaching effect, due to adsorption by the catalyst of the traces of organic colouring matters present in the fat, or to their hydrogenation to colourless derivatives. The hydrogenation action is strongly exothermic in character and it is frequently necessary to cut off all supply of heat once the action has set in, and it may even be desirable in the case of very refined oils to control the temperature by passing cold water through the jacket or internal coils, or by cutting down the flow of hydrogen, in which case the rate of hardening of the charge is also slowed down.

Complete saturation of a fat is not often desired and the progress of the hydrogenation is followed by determinations of setting point or iodine number on small samples withdrawn from a sampling tap, or more rapidly and accurately by noting the alteration in a suitable physical property, the refractive index being most adapted to the purpose.

Circulatory System.—The plant employed in this case also consists of a cylindrical shell, usually, however, wider in proportion to its height than in the agitator plants. In this system the hydrogen is not passed through the oil, but forms an atmosphere above the latter, and consequently it is admitted by a pipe communicating with the lid of the vessel. A similar connection is also provided on the lid with a safety valve and blow-off pipe.

From near the bottom of the vessel there leads a pipe connected to a pump which continuously removes oil and catalyst and delivers it through a further pipe which passes through the side of the vessel near the top, and terminates in a spray nozzle directed towards the inside of the lid.

In operation, a charge of fat containing from 0·1 to about 0·3 per cent. of metallic nickel is pumped into the vessel, the charge occupying about two-thirds of the volume of the vessel. The proportion of catalyst is best kept fairly low in this process in order to facilitate the circulation. The gas space above the fat is filled with hydrogen and the charge heated up to temperature by steam jacket or internal closed steam coils as in the system described above. The oil and catalyst charge is then continuously circulated by means of the pump and delivered into the gas atmosphere in the form of a fine spray.

The process is usually conducted under considerably higher pressure of hydrogen than the agitator system, namely, from about 8 to 12 atmospheres; any impurities present in the hydrogen tend to accumulate in the closed gas space, and it may be necessary periodically to discharge the latter and re-fill with fresh hydrogen. The actual pressure at which the oil and catalyst is sprayed into the

reaction chamber, on the other hand, is not very great and is governed mainly by the degree of fineness of the spray nozzles. The charge should be completely circulated about 10-20 times per hour. This system avoids the difficulties inherent in the gland-packing necessary with a mechanical agitator, which are somewhat troublesome when dealing with oil and hydrogen at a high temperature ; but it has the disadvantage of necessitating a closed gas system which involves the accumulation of gaseous impurities, which retard the rate of hydrogenation even if these latter are not toxic to the catalyst. Consequently the circulatory system works best with very pure gas, such as electrolytic hydrogen.

In either system, when the oil is sufficiently hydrogenated, the charge is cooled to about 100-120° C. and pumped through a filter-press in order to separate the oil and the catalyst. The oils should thus be obtained quite free from catalyst and ready for use, whilst the residual catalyst, which usually retains at least its own weight of adherent fat, may usually, if the oil treated has been of fair quality, be employed in the hydrogenation of further batches of oil before it becomes spent. After it has become deactivated to an extent which renders it inefficient in hydrogenation, the adherent fat may be removed by extraction with benzine or similar solvent, and the nickel recovered by solution in sulphuric acid ; the nickel sulphate so obtained is utilizable in preparing fresh catalyst and so, theoretically, the nickel employed need not be lost and may be considered as a capital charge.

Continuous System (Bolton and Lush).—This method is distinct from the others described in several respects, and is designed to work continuously, that is, to maintain a constant feed of raw fat and withdraw a constant stream of hardened fat. To this end the catalyst used is in a special compact form and is, in fact, a mass of fine nickel turnings or nickel wool supported in a suitable nickel framework which is held in a vertical steel tube, the latter being electrically heated externally. As already indicated, massive

nickel of this kind has negligible catalytic power, but the inventors of this process have found means to obtain a sufficiently catalytic surface on the nickel either by immersing it as the anode in a dilute solution of sodium carbonate which is being electrolysed at a suitable current density, or by immersing it in a bath of dilute sodium hypochlorite of specific concentration. By either method the nickel is superficially coated with an adherent film of oxide, and, after washing and drying, is replaced in the hydrogenation vessel and heated at about 250° C. in hydrogen, when it becomes catalytically active.

The oil to be hydrogenated is admitted at the top of the closed hydrogenation vessel fitted with the nickel cage, and trickles down over the catalyst at about 170–180°, where it meets a current of hydrogen delivered at the base of the vessel. A large-scale plant consists of several of these units, through which the fat is made to flow in series. The excess of hydrogen is collected from the tops of the vessels, whilst the hydrogenated fat collects at the bottom and is continuously withdrawn through a seal pipe. When the catalyst becomes spent, it is washed with petrol to remove adherent fat and re-submitted to either of the surface oxidation processes, washed and dried and re-reduced. All these operations should, if possible, be arranged to be carried out in one and the same vessel, in order to bring the process to maximum efficiency. Separation of the hardened fat from catalyst by filtration is unnecessary in this process.

"Conjugated hydrogenation."—A certain amount of attention has been given in Russia of late years to fat hydrogenation so as to avoid the use of gaseous hydrogen. It has long been known that, in presence of nickel or other catalyst, hydrogen can be transferred from a compound which is easily dehydrogenated to an unsaturated compound also present in the system. Ljubarski proposed in 1932 to treat a mixture of cottonseed oil and ethyl alcohol with nickel catalyst in this way. The process is carried out at about 250° and at a pressure of 25–30 atmospheres; hydrogen is removed from the alcohol (with production of alde-

hyde) and added to the unsaturated fat. The production from sunflower seed oil by this means of products similar to olive or groundnut oils has been described. The system reaches an equilibrium point and the iodine value of an oil cannot apparently be reduced to below about 70 by this process. Propyl or hexyl alcohols have been mentioned as alternatives to ethyl alcohol. It is doubtful whether this so-called "conjugated hydrogenation" has much more than theoretical interest.

Properties of Hydrogenated Fats and the Course of the Hydrogenation Reaction.—Hydrogenated fats from different oils show specific differences in character, so that particular oils may often be selected in order to yield products with a particular combination of properties. This may be illustrated by comparison of the chemical composition of a hardened whale or fish oil with a hardened linseed or soya bean oil: in the former cases, apart from the various hydrogenated glycerides present, the glycerides are composed of fatty acids containing either 14, 16, 18, 20, or 22 carbon atoms, whereas in the latter over 90 per cent. of the fatty acids present contain 18 carbon atoms, and so the fat is continually approaching nearer to simple tristearin the further it is saturated. Consequently it is natural that the melting points of completely saturated fats vary widely, as may be shown by the following typical figures:

Completely hydrogenated :						M.p.
Coconut oil	43-45°
Palm kernel oil	43-45°
Herring oil, cod oil	52-55°
Whale oil	54-56°
Palm oil	*	56-58°
Cottonseed oil	62-63°
Olive oil, groundnut oil	68-69°
Soya bean oil, linseed oil	69-71°
Castor oil	86-90°

On the other hand, over the range of products in ordinary technical use, and for the oils mainly employed in hydrogenation (*i.e.* whale, fish, linseed, soya bean, cottonseed, etc., oils), the consistency and melting point of the

hardened fats may approximately be correlated with their degree of unsaturation as follows :

Iodine value of hardened oils.	Consistency.
80-90	Semi-liquid, thin pastes.
65-80	Soft pastes, m.p. 30-35° C.
50-65	Soft tallows, m.p. 35-45° C.
35-50	Hard tallows, m.p. 45-52° C.
20-35	Very hard tallows, m.p. 52-55° C.

There are two factors connected with the course of hydrogenation which have a most important bearing on the applications of hardened fats, namely, the *selective nature* of hydrogenation and the production of glycerides of *solid unsaturated acids* during hydrogenation.

Selective Hydrogenation.—If a mixture of linolein and olein is hydrogenated, it is found that the linolein is practically entirely transformed into olein before any of the latter is converted to stearin. This principle applies throughout when unsaturated fats are hydrogenated, so that, in simplest terms, it may be said that any oil, e.g. cottonseed, linseed, soya bean, whale oil, etc., is hydrogenated so that all glycerides less saturated than olein (or mono-ethylenic glycerides) are transformed to the latter before any material increase in the glycerides of the saturated fatty acids occurs.

This remarkable fact, which should be considered in conjunction with the views given in the early part of this chapter on the association between active catalyst atoms and unsaturated centres, was first pointed out by Moore, Richter, and van Arsdel in the case of cottonseed oil, and was also noted in this case and with other vegetable oils by Richardson, Knuth and Milligan, and by C. W. Moore and Hilditch. Richardson and his co-workers subsequently showed that the highly unsaturated glycerides of marine animal oils pass direct to the linolein, or di-ethenoid stage, and then apparently to the fully saturated acids simultaneously with the production of mono-ethylenic derivatives. Later work by Hilditch and collaborators has served to confirm and amplify the conclusions of these investigators, and to indicate that, in the continuous process, the operative mechanical conditions cause alterations in the amount of

selective action, which reaches a maximum as the mixture of fat and catalyst approaches complete homogeneity (intensive agitation). The more recent work has also shown that triolein passes to stearodiolein more rapidly than the latter to oleodistearin, or than oleodistearin to tri-stearin, although all these three stages may take place concurrently.

The selective character of the process has obvious important practical implications, the first of which is that, except over a very narrow range, the composition of a hardened fat of given iodine value (say 50) may not be reproduced by mixing a much less hardened with a much more hardened fat (*e.g.* one of 90 with one of 10 iodine value). The proportions of fully saturated, mono-ethylenic, and polyethylenic glycerides present will not necessarily be the same in both cases.

A further most important feature is that for many purposes the presence of glycerides more unsaturated than olein is undesirable, since these are much more prone to change by atmospheric oxidation and by the development of rancidity. Therefore oleins, or rather, liquid mono-ethylenic glycerides, are the most valuable components of soft oils which are to be transformed either into edible fat or soap, or which are to be employed as high-class lubricants, and it is thus a fortunate circumstance that the process is so markedly selective; if linolein or less saturated glycerides passed directly to stearin, it might well happen that a very hard fat still contained appreciable quantities of glycerides more unsaturated than olein.

Unfortunately, however, this advantage is somewhat clouded by the fact that the mono-ethylenic or "oleic" glycerides produced from the less saturated derivatives are not all liquid; thus when linolein is semi-hydrogenated the product is a mixture of several oleins, some of which are solid. For reasons about to be described hardened fats containing these solid or "iso-oleic" derivatives are not quite so adapted for various purposes as they would be were all the olein present liquid at the ordinary temperature.

Production of Solid Unsaturated Acids during Hydrogenation.—Since the ethylenic linkages in a highly unsaturated fatty acid occur at different points in the chain of carbon atoms, it is easy to understand why the oleic acids produced by selective hydrogenation are not all the same and identical with ordinary oleic or $\Delta^{9:10}$ -octadecenoic acid—the double bond left unsaturated may equally well be one of the others. This is the chief cause of the occurrence of solid "iso-oleic" acids in the glycerides of partially hydrogenated oils, but there is also another means whereby they are produced during the hydrogenation of esters of oleic acid itself. Moore showed that in the latter process there are produced, in addition to stearic derivatives, esters of elaidic acid (the solid geometrical isomeride of ordinary oleic acid) and of another solid iso-oleic acid ; Hilditch and Vidyarthi found that, in fact, liquid and solid forms of the octadecenoic acids with double bonds adjacent to those in oleic acid ($\Delta^{8:9}$ - and $\Delta^{10:11}$ -octadecenoic acids) are produced, as well as elaidic acid, but in smaller proportions.

This is incidentally one of the earliest and most definite chemical proofs of the intimate association between catalyst and unsaturated organic compound, for, as Armstrong and Hilditch pointed out, it becomes evident that the oleic centre of unsaturation is so affected that it is in part isomerized to the stereo-isomeric form ; and elaidic ester similarly passes over partially to the liquid oleic form during hydrogenation. Further, the displacement of the ethylenic linkage along the chain of carbon atoms again stresses the far-reaching influence of the catalyst on the organic compound.

Whilst the formation of iso-oleic derivatives has thus profited the theory of the process, it is unfortunately only a disadvantage from the practical standpoint. It may be pointed out that less of the solid iso-oleins tends to be produced at lower temperatures of hydrogenation than at higher, and thus (to some extent only) their proportion may be diminished by operating at a lower temperature than that at which the action proceeds most rapidly.

The practical objections to the presence of iso-oleins are

not so much their higher melting point, although this of course tends to make a hardened fat of given iodine value possess a higher melting point than a natural fat containing the same proportions of liquid oleic and saturated acids in its mixed glycerides.

The crystal structure of the solid iso-oleins, which is usually that of large, soft, waxy plates, tends to affect the appearance and consistency of edible fats in which they may be present and introduces some difficulties in cooling and preparing the final product.

Similarly, the crystal structures of the corresponding iso-oleic acids are less tractable than that of palmitic and stearic acids, and this complicates to some extent the problem of utilizing fatty acids from hardened fats in the candle industry.

The most objectionable properties of these acids are, however, connected with their behaviour as soaps: whereas oleic acid is an almost ideal constituent of soap by virtue of the relative solubility and low surface tension of solutions of its sodium salt, the solid isomeric oleic acids yield sodium salts of lower solubility and much higher surface tension. In practice this means, as is described in Section V., Chapter II., that these soaps are inferior in lathering and detergent power to soaps made from natural fatty acids of the same degree of unsaturation. This disadvantage can, however, be largely remedied by adjusting the composition of the soap-charge so as to include a higher proportion of the natural liquid fats, and what has been said above must not be taken to indicate that the use of hardened fats in soap, edible fats, or candles is unduly restricted. It is intended rather to convey the impression that, were only liquid oleins produced by the hydrogenation process, a complete simulation of almost any natural fat other than the nut oils would have been rendered possible, and in this case the value of the process would have been even greater than it is. As it stands, fat-hydrogenation is capable of controlling the price and output of the harder natural fats (tallow) to a very marked degree.

Furthermore, it should be pointed out that considerable prejudice has been manifested from time to time against the employment of hardened fats in edible fats and in soap, and that much of this is, in the writer's opinion, quite unwarranted and goes beyond the admitted differences in properties between hardened and natural fats. An attempt has been made above to give a reasoned statement of those differences which do exist in fact.

As regards colour, hydrogenated fats are usually superior to many natural fats, either as fat or as soap ; and whilst objections were formerly raised to a specific odour associated with soaps or fats containing hydrogenated material, it is correct to say that by adoption of due precautions in the treatment of the oils during hydrogenation the products are almost completely odourless, and the very faint characteristic odour sometimes observed is by no means unpleasant. Quite probably any difference in odour of soaps from natural and hydrogenated sources is as much due to lack of characteristic odours from the natural fats as to added odour due to hydrogenated material.

Production of Higher Fatty Alcohols by Hydrogenation of Fatty Acids or Oils.—If fats are subjected to the action of hydrogen in presence of an appropriate catalyst at 200–250° and at very high pressures (100–200 atmospheres) a kind of hydrogenation entirely different from that discussed in the previous pages sets in, namely, reduction of the carboxylic or ester group to the corresponding alcohol (or even paraffin hydrocarbon). Until this catalytic process was discovered (about 1930) the only method available for the production of the higher fatty alcohols was by reduction of the corresponding esters with sodium and alcohol by the method of Bouveault and Blanc. Higher fatty alcohols are in demand nowadays, not only for waxes, but mainly because their hydrogen sulphates and hydrogen phosphates give alkali salts which possess very valuable properties as detergents, emulsifiers, wetting-out agents, etc. (see Section V., Chapter VII., p. 401). Their technical production has thus become of considerable importance.

The technical procedure is to reduce fats or fatty acids at the temperatures and high pressures indicated in presence of reduced basic copper chromate as catalyst, the hydrogenating catalyst being thus copper instead of nickel. It was developed mainly by Schrauth, Böhme A-G and the Deutsche Hydrierwerke A-G. The reduced "copper chromite" is mixed with the fatty oil and subjected to the action of hydrogen at 150–200 atmospheres at about 200°. The carboxylic groups are quantitatively reduced to the corresponding alcohols, whilst ethylenic unsaturation originally present may or may not disappear. As a rule, under the conditions mentioned, a considerable proportion of any oleo-glycerides in the raw material appear in the product as oleyl alcohol.

Adkins and co-workers have pointed out that it is essential to use a copper catalyst in order to obtain high yields of alcohols, and that substitution of nickel for copper catalyst leads to the further reduction of considerable proportions of the alcohols to long-chain hydrocarbons and methane.

By the technical process, coconut and palm kernel oil yield a mixture of alcohols containing about 50 per cent. of dodecyl or lauryl alcohol; tallow, lards, or palm oils similarly give a mixture of cetyl and octadecyl or oleyl alcohols; whale oil or fish oil a mixture containing a little tetradecyl with something like equal proportions of cetyl, octadecyl, eicosyl, and docosyl and corresponding unsaturated alcohols; and so on. The composition of the mixture of alcohols obtained from any fat naturally depends upon the proportions of the corresponding fatty acids originally present. By fractional distillation under reduced pressure the individual alcohols may be separated from each other more or less completely.

CHAPTER IV.—FAT-SPLITTING OR HYDROLYSIS

Introductory.—The soap, glycerine, turkey-red oil, leather, candle, and some other industries with which this book is concerned require one or other of the component parts—fatty acids or glycerol—of the neutral fat and not the latter as such. The operation of fat-hydrolysis, or resolution of the fatty esters into the component acids and alcohol, is thus one of fundamental importance in the industry, and, following the general scheme of the present volume, the chief methods used in technical practice are collected in the present chapter.

According to the end in view, various modes of procedure are adopted. The simplest and probably the most widely used method is that of saponification with an aqueous solution of caustic soda, employing the latter in amount equivalent to the fatty acid present. This transforms the fat almost quantitatively into soap and is the method almost always employed in large works in soap manufacture. It furnishes the glycerine in the form of a very dilute solution or lye, which requires concentration; the evaporation of such dilute glycerine solutions can only be carried out economically in very large installations, and therefore this encourages small soapmakers to employ other methods of hydrolysis.

Occasionally a fat is hydrolysed primarily for its glycerine content, and in a number of other cases the fatty acids are required as such, and not as soap. In these circumstances other technical methods of hydrolysis are available, which have the advantage of producing the fatty acids directly and at the same time furnishing a much more highly con-

centrated glycerine liquor than is available from the soap pan. These methods include the hydrolysis of fats by lime instead of soda, by water at about 120–150° C. in autoclaves in presence of small amounts of certain oxides, by water at about 80–100° C. in presence of a special agent known as the Twitchell reagent, by water in presence of the enzyme lipase, and by concentrated sulphuric acid.

The modern advantages of plant capable of withstanding high pressures have permitted the introduction of new methods in fat hydrolysis, including processes for continuous saponification by caustic alkali, for continuous hydrolysis by water alone, and for splitting by the autoclave process in presence of water without the addition of lime or other oxides.

Saponification Processes.*—(i) *Aqueous Caustic Soda (or Potash)*.—As stated, this is the process most commonly used in the large-scale manufacture of soap. It is carried out in large open vessels known as soap pans, which may vary from about 10 to about 200 tons total capacity and are usually constructed of steel plate, rectangular or square in section, more rarely cylindrical, with a shallow tapered base terminating in a draw-off pipe which may be 4–6 inches in diameter. The pan is equipped with a flat coil over the base of the vessel containing numerous perforations for the passage of open steam into the soap charge; a second, closed steam coil extending about one-third up the pan is sometimes, but not usually, also fitted. The pan is provided with a skimmer pipe which can be raised and lowered so that finished soap can be pumped off from any level. Delivery pipes for conducting water, caustic liquor, fat, and brine into the pan complete the essential fittings.

The actual charge of finished soap will only be about two-thirds of the total capacity of the pan, and as this soap contains about 63 per cent. of fatty materials the charge of fat introduced originally will be about half the capacity of the pan.

* For theories of the mechanism of aqueous saponification of fats, see Section V, Chapter II, p. 349.

The fat charge, proportioned from various sources, natural or hydrogenated, according to the nature of the soap to be produced (*cf.* Section V., Chapter I.), is run into the pan in the liquid state and heated to about 100° C. by means of the open steam coil, whilst caustic soda solution of 1·1-1·2 specific gravity (20-40° Tw.) is simultaneously and cautiously added in small proportions, the passage of steam being continued so that the mass is kept thoroughly agitated and in a state of gentle ebullition. If the correct local concentration of caustic liquor is present the whole mass of fat, water, alkali, and soap is maintained in a homogeneous emulsion; addition of too much caustic liquor at a time tends to break the emulsion, and saponification does not proceed at the maximum rate. By gradual addition of the liquor and experienced control of the current of steam, however, the hydrolysis takes place very rapidly and the addition of caustic liquor is completed within a few hours. The amount of liquor employed must be very slightly in excess of that theoretically necessary for complete saponification; the latter amount is known from the weight and mean saponification equivalent of the fat charge, and the total caustic liquor to be given to the pan is determined accordingly.

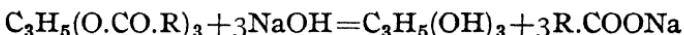
The soapboiling is continued for some hours after all the alkali has been added, but the saponification is usually complete in from 12 to 24 hours. Completion of hydrolysis (the soap being "up to strength") is judged by the taste of the soap, by the use of litmus or alkali-blue test papers, or by the "brightness" of the soap; presence of neutral fat is usually betrayed by a dull appearance in the soap.

Caustic soda is the alkali most frequently employed in soap manufacture, but for a few special purposes potash soaps are produced technically, and in such cases of course the alkaline liquor used consists of caustic potash.

When saponification is complete, the contents of the pan are boiled up more freely and thoroughly agitated with open steam, and brine is added cautiously until the soap separates in the form of a thick curd; only the mini-

mum amount of brine necessary to effect this separation should be employed, in order to obtain the greatest possible removal of glycerine lyes from the soap curd. The contents of the pan are then left to settle for a few hours and the lower layer of aqueous liquid is drawn off : this contains, in addition to salt, traces of organic matter and excess of alkali, nearly all the glycerine originally present in the fat.

The operation has proceeded according to the equation :



The soap thus produced in the form of curd is still not sufficiently pure to be made up into household or other commercial soap, and its further treatment to this end, which is definitely a feature of the soap industry rather than of fat-hydrolysis, is dealt with in Section V. (pp. 339-347).

The lyes contain about 3-7 per cent. of glycerine and are pumped to settling tanks in which traces of soap are collected, and subsequently dealt with as raw material in the production of glycerine (Section VII., pp. 425-428).

Saponification Processes.—(ii) *Continuous alkali saponification process.*—As in alkali refining of fats (p. 233), so in alkali saponification continuous systems of working have been introduced, and in some factories, notably in the United States, rapid continuous processes have been introduced as alternatives to the soap pan. The fats are emulsified thoroughly with the theoretical proportion of caustic soda, or of sodium carbonate, solution and are then passed under a pressure of 50-100 atmospheres through a small-bore reaction tube, part of which is maintained at a temperature of about 300°. The actual period of saponification of the material at this temperature is only 30 seconds, and the extruded material is cooled and converted into powdered soap by spray drying. It may well be that processes of this nature will come into increasing use in the saponification of fats for the manufacture of soap powders.

Saponification Processes.—(iii) *Milk of Lime.*—In small soap and candle works such as are still largely in operation in many parts of the Continent it is not customary to

deal with the recovery of glycerine in the works, but to despatch the lyes elsewhere to be concentrated. To this end it is desirable to obtain as high a glycerine concentration as possible, and, although this can be effected by the autoclave or Twitchell methods as described subsequently, it is also possible to attain this end in an open soap pan if lime is used as the hydrolytic agent. Saponification with milk of lime is therefore convenient in small factories, both on account of cheapness of reagents and of the plant required, and of the more concentrated glycerine lyes available ; also, the colour of the soap or fatty acids is as good as that obtained in the ordinary soap pan with soda, and is as a rule superior to that from autoclave or Twitchell hydrolysis. It is also claimed that coloured impurities are absorbed by the calcium carbonate or sulphate formed during conversion of the resulting lime soap respectively to soda soap or free acid, and that accordingly better-coloured products may frequently be obtained from low-grade oils than by soda saponification, especially if the Krebitz lime soap process is employed. Improvement in the colour of the final soda soaps or fatty acids is not, however, always obtained to a marked extent, although in individual cases this may take place.

The saponification may be conducted in an open soap pan as in the soda process, agitation being carried on by open steam and a thick cream of slaked lime and water being slowly added until about 50 per cent. excess of the alkali necessary for complete conversion of the fat to lime soap is present. After about twelve hours, saponification is complete and the lime soap separates as a curd, is allowed to settle, and the aqueous lyes drawn off ; the lime soap curd is washed once by boiling with water by means of the open steam and again settled. The further treatment of the lime soap depends on the use to which the fatty acids are to be put : for soap purposes it is boiled with a solution containing the equivalent amount of sodium carbonate, and the calcium carbonate produced separates in the lyes when the soap is "grained out" with lime as a curd in the

usual way, and carries with it a certain amount of adsorbed impurities. If the fatty acids are required as such, the lime soap is boiled in wooden vats with dilute sulphuric acid and the fatty acids collected by settling and skimming or running off.

The more modern form of this method, known as the Krebitz process, is intended to economize in the steam used for agitation and also to produce glycerine liquor of a higher concentration and, possibly, fatty acids improved in colour. The lime and water (in 50 per cent. excess as before) are added to the fat at about 40–50° C., and the mixture is then carefully agitated with steam until it is just converted into a stable emulsion, the temperature of which is not allowed to reach more than 90–95° C. The contents of the pan are left for about a day during which complete, or almost complete, saponification occurs, leaving an almost solid mass of soft lime soap, water, and glycerine which is ground to a friable powder, and then washed with the smallest quantity of water requisite to remove the glycerine. The glycerine liquors are then ready for glycerine recovery, either in the same works or at a convenient centre, whilst the washed lime soap is converted as above either into soda soap or into fatty acids for candle-making or other purpose.

As already indicated, either form of the lime saponification process finds little application at present in the English industry.

The Autoclave Process.—When fatty acids rather than soaps are being manufactured, it is clear that the expense of caustic soda could be avoided if water alone were employed as hydrolytic agent; and, even for soapmaking, the caustic soda could thus be replaced by the cheaper soda ash, which could then be used to neutralize the liberated fatty acids in a subsequent process.

The statement is sometimes met with in general textbooks of organic chemistry that fats are most frequently hydrolysed by the use of superheated steam alone, but this is hardly correct. Probably over 50 per cent. of the fat

hydrolysed in this country and elsewhere is directly converted into soap in the open pan.

Hydrolysis by water alone requires so high a temperature (about 200–220°C.) before it proceeds at a technically useful speed that until recently this was not a feasible technical process. Developments in construction of high pressure vessels and in the acid-resisting steels now available for chemical plant have, however, materially altered the situation.

It has long been known that a small proportion of certain basic oxides, especially lime, magnesium, and zinc oxide, exerts a strong catalytic acceleration upon the rate of hydrolysis, and this has been taken advantage of in practice in such a way that the process can be completed at about 140–150° C. (100–120 lbs. per sq. in. steam pressure) in presence of a catalytic base, in the same time as that necessary at 250 lbs. per sq. in. or higher pressure of steam alone.

The process in this form has been fairly widely used, more especially when the fatty acids are required as such. The advantages gained are the elimination of the relatively costly caustic soda on the one hand, and on the other, the production of a much more highly concentrated glycerine lye; the "sweet waters," as the aqueous liquors from non-alkaline hydrolysis of fats are sometimes termed, may contain up to about 15 per cent. of glycerine.

The operation is usually conducted in stout vertical cylindrical vessels with rounded ends, either jacketed or fitted with an internal closed coil. The autoclave is preferably constructed of copper in order to minimize discolouration of the fatty acids by metallic soaps, and sometimes, but not invariably, is fitted with a mechanical agitator. The main agitation is effected, however, by a current of steam which is distributed into the base of the charge of fat and water by means of a perforated pipe; a certain amount of steam is continuously withdrawn from the top of the vessel by an exit valve which may be fitted on the same connection as the safety-valve and pressure-

gauge, and this causes agitation to be maintained by the automatic admission of fresh steam to maintain the pressure.

The vessel is charged to about 70–80 per cent. of its capacity with a mixture of about 80 per cent. of the fat to be hydrolysed, 20 per cent. of water and about 3 per cent. of lime, or a mixture of lime with some zinc dust is added. The object of the zinc dust, which is a mixture of oxide and metal, is partly to act as hydrolytic catalyst and partly to aid in preserving the fatty acids from discolouration ; this is probably effected by the reducing action of the metallic zinc. It will be observed that the amount of "catalytic" base which experience has shown to be advisable is about 30 per cent. of that necessary to neutralize the total fatty acid produced, and is thus by no means a negligible proportion, although of course it represents a saving of over two-thirds of the alkali which would otherwise be required.

Steam is then admitted to the closed autoclave, which is kept at a pressure of 100–120 lbs. per sq. in. for 10 or 12 hours. The hydrolysis, in accordance with the law of mass action, proceeds at a rate which is approximately proportional to the amount of unsaponified fat present at a given time. Thus, 90 per cent. of the fat is usually hydrolysed in the first 3 to 5 hours, but conversion of 98–99 per cent. of the fat to fatty acids requires, as stated, 10 to 12 hours.

The process is usually continued, however, until the conversion to fatty acid approaches 98 per cent. When samples withdrawn from the charge show that this is the case, it is usually blown into a separate wood-lined tank or vat (which should be well lagged externally) in which it is left to settle for some time, after which the lower layer of aqueous liquor or "sweet water" is drawn off and dealt with for glycerine recovery.

The upper layer is then boiled up by means of steam, when sufficient dilute sulphuric acid is added to neutralize the lime soap present, and the fatty acids are settled and skimmed or run off.

High pressure hydrolysis by water alone.—The increased

boiler pressures of 250 lbs. per sq. in. and higher now available in steam-raising plants, and the provision of acid-resisting steel vessels capable of withstanding high pressures, have caused the older forms of the autoclave process described above to be superseded in part. In the plants now referred to, the fat is mixed with water in a high-pressure vessel fitted with closed steam heating coils and also with provision for admission of jets of steam to provide agitation and thorough mixing. The vessel is heated by steam at or above a pressure of 250 lbs. per sq. in. and the contents, whose temperature reaches 200–220°, are agitated by injection of a certain proportion of steam, when hydrolysis proceeds sufficiently rapidly in the absence of any lime or similar catalyst.

The process is made more rapid by operating it in two stages. In the first stage the action is allowed to proceed until 50–60 per cent. of the fat has been transformed into free fatty acid. It is then interrupted, the "sweet water" drawn off from the partly hydrolysed fat, and the process resumed after adding more water to the latter.

Hoffmann has proposed a continuous form of high-pressure hydrolysis in which the products are immediately separated by fractional condensation. The fat is first refined with bleaching earth and then emulsified with water and passed through a "splitting zone" at 220–260° under 20–60 atmospheres pressure. The reaction is almost instantaneous and the products are expanded into a high-vacuum zone where fatty acids and glycerol pass into the vapour phase, leaving unhydrolysed fat (1 per cent.) and unsaponifiable matter in the liquid phase. Fractional condensation of the vapours yields, first, the fatty acids and next, most of the glycerol as an 80–90 per cent. solution. Reports of the large scale working of this process have not yet been given.

The colour of autoclaved fatty acids is always somewhat damaged, even under the relatively low temperature conditions (140° C. or thereabouts) which are employed in the process first described. This factor rather militates against

the use of the autoclave process for fatty acids for soap-making, but is not so serious a matter for the candle or oleine industries (Section VI., p. 413). Here the autoclaved acids are first distilled in a vacuum, the products from a modern plant being quite pale-coloured ; the distilled acids are then separated into "stearines" and "oleines" by chilling and pressing.

The Twitchell Process.—This process consists in the catalytic hydrolysis of fats by an "artificial ferment" first patented by Twitchell, who prepared it by acting on a solution of oleic acid in benzene or preferably naphthalene with sulphuric acid. Sulphonation and condensation take place and the resulting product appears to be of the general type $\text{COOH} \cdot \text{C}_{17}\text{H}_{34} \cdot (\text{C}_{10}\text{H}_6) \cdot \text{SO}_3\text{H}$ (taking naphthalene as the aromatic constituent).

M'Kee and Lewis recommended *p*-cymene sulphonic acid instead of naphthalene sulphonic acid on the grounds of more rapid action and less discoloration in the products. The Vereinigte Chemische Werke ("Pfeilring") produced a similar agent from hydrogenated castor oil acids with naphthalene on sulphonation for the same reason of improvement in colour of the split fatty acids. Other "contact agents" which have been proposed are "Idrapid" (octahydroanthracene sulphonic acid), "Nekal" (1-*iso*-propyl, butyl-, or other alkyl-naphthalene sulphonic acid) and "Kontaktspalter" (a sulphonated fraction from petroleum refining).

The mode of action of these reagents is fairly clear in view of the present knowledge of the orientation of molecules in adsorbed films. It is quite evident that a compound of the type given when distributed in a fat-water system will arrange or orientate its molecules so that the aliphatic part of the chain is directed towards the fat, and the acidic radicles, especially the sulphonic group, towards the water.

When the fat and water are intimately mixed or emulsified, therefore, molecules of water and of fat will actually form part of the same system (fat-contact agent-water),

and in presence of the strongly acidic sulphonic group hydrolysis is effected.

The agent is thus a close artificial or synthetic reproduction of a typical hydrolytic enzyme, and this is emphasized by the fact that its action is reversible—glycerine and free fatty acids can to some extent be combined into neutral fat when the agent is allowed to interact with fatty acid and excess of glycerol.

In practice the agents are employed in about $\frac{1}{2}$ -1 per cent. concentration on the fat present.

The process is best carried out in a wooden vat with a loose lid and containing a perforated copper coil for the admission of steam. The fat-charge, previously well clarified by boiling with dilute sulphuric acid and settling, is placed in the vat with about 50-100 per cent. of its weight of water and a small proportion of the contact agent as stated. It is heated to 100° C. and maintained in gentle ebullition throughout the process by open steam. After a shorter or longer period of induction, hydrolysis sets in and proceeds fairly rapidly at first, and progressively more slowly as the concentration of neutral fat diminishes. The process may require 24-60 hours to complete; it is usefully accelerated by intercepting when about half the fat is hydrolysed, settling and running off as much glycerine liquor as possible, adding more water to replace the latter and resuming the hydrolysis.

When a 97-98 per cent. conversion to fatty acids is reached, the mixture is boiled with a little sulphuric acid until all emulsion has disappeared, settled, and the fatty acid lye washed by boiling with water.

The advantages of this process are its cheapness in reagents and in consumption of steam; it has compensating disadvantages in the somewhat lengthy period of hydrolysis and in a tendency to the production of dark-coloured fatty acids. The glycerine concentration of the aqueous liquor is fairly high and may approach that obtained in the autoclave process.

The Twitchell method is used fairly extensively in

America and to a less extent on the Continent, but does not appear to make very great headway in England.

The Lipase or Fermentation Process.—This method, like the preceding one, is catalytic, but depends on the use of a natural hydrolytic enzyme, lipase. It yields excellently coloured fatty acids, and glycerine liquor of very high strength (up to 16–17 per cent.) may also be obtained. The process will probably find much wider applications when methods of producing the enzyme in a more stable state, less sensitive to the exigencies of working conditions, have been worked out, together with means for avoiding undue emulsification when the hydrolysis is completed and for minimizing the organic water-soluble impurities which are at present produced in the glycerine liquor.

The enzyme lipase is widely distributed in nature and occurs in vegetable seeds. It is particularly abundant in castor seeds, which are usually made the source of the lipase used in technical fat-splitting.

Castor seeds are decorticated, carefully separated from fragments of husk and extraneous matter as described on p. 200, and then passed through a series of rolls in which they are ground to a fine meal which is intimately mixed on a perforated shaking screen with sufficient water to form a thick paste. This is centrifuged to separate the seed particles from the "seed milk" or aqueous emulsion; the latter is set aside for a day or two at about 23° C., during which fermentation sets in and the pasty emulsion separates into an aqueous layer and an upper layer resembling thick cream. The latter consists of an aqueous emulsion of castor oil fatty acids, holding the lipase in suspension, and is used as the hydrolytic agent.

The activity of the agent varies somewhat widely in different preparations, and it is desirable for further investigation on this subject to be pursued in order to overcome this tendency to irregularity. It has been suggested that the presence of a small proportion of sulphates of calcium or manganese in the ferment both activates and stabilizes the preparation.

The actual fat-hydrolysis should be carried out after thorough boiling of the raw fat with dilute sulphuric acid, followed by settling and thorough washing ; this precaution is even more important here than in the Twitchell process.

The fermentation is effected in wooden vats fitted with a perforated copper coil at the base for the admission of air, which is used as a means of agitation. The operation should be carried out in a room the temperature of which is always between 20–30° C., this being the most effective range in which the enzyme acts.

The process, accordingly, is best suited to soft oils ; tallow and harder fats cannot conveniently be handled unless by admixture with a liquid fat they have been brought to a semi-solid consistency at 20–30° C.

The fat to be hydrolysed, with up to half its weight of water and about 7–10 per cent. or more of added ferment-cream (according to its degree of activity), is churned up by agitation with air until a stable emulsion is just produced. It is then left to stand until hydrolysis is sufficiently complete ; this usually requires about one day with a very active lipase, or longer with less efficient preparations.

When the hydrolysis is completed the emulsion is broken as much as possible by agitation with steam, which may be admitted through the same coils ; a small amount of sulphuric acid may also be added, but it is well to avoid this if possible. The mass separates on settling into a fatty acid and an aqueous layer with an intermediate layer of emulsion, and it is a matter of manipulation to ensure that this is as small as possible. The clear layers are separately drawn off and the emulsified layer steamed with dilute sulphuric acid in order to recover more fatty acids. The clear fatty acid layers are re-washed twice by cautious agitation with steam.

The lipase fat-splitting process is a step in the right direction in that it is an attempt to utilize Nature's active chemical agents—the enzymes which by operating at normal temperatures avoid the unnecessary expenses of fuel for steam and of manufactured chemicals as reagents.

The Acid-hydrolysis Process.—The saponification of fats by strong sulphuric acid has long been technically employed in some cases in the candle industry and in manufacturing fatty acids from low-grade material such as bone fat. Under these conditions loss of glycerine occurs by dehydration and oxidation, and therefore the method is only employed as a rule at the present day for dealing with materials which in any case would furnish glycerine in too impure a condition to be of technical value. It will probably become more and more replaced by pressure hydrolysis followed by distillation of the resulting fatty acids.

The process depends on the partly hydrolytic, partly sulphonating action of strong sulphuric acid. The crude fat is first of all completely dried by heating to a temperature well above 100° C., and is then intimately mixed with about 5–8 per cent. of concentrated (96 per cent.) sulphuric acid, and heated with mechanical agitation and admission of dry steam until hydrolysis is complete. The process is usually carried out at about 110–120° C., and may require 8–12 hours for completion.

As would be anticipated, the resulting fatty acids are extremely dark in colour and are of no value as produced. They are cleansed from sulphuric acid by boiling with water two or three times, after which the layer of fatty acids is separated and distilled.

The distillation is carried out in a cylindrical vessel which is gas- or fire-heated. A current of high-pressure steam, superheated to about 300° C., is passed into the fatty acids through a perforated pipe at the bottom of the still, and the fatty acid vapours are condensed in air-cooled lead coils. This represents the oldest form of fatty acid distillation plant.

In modern plants reduced pressures are employed, and the distillation can be carried out at a much lower temperature. The colour of vacuum-distilled oleine is naturally much better than that from the older processes, especially if modern acid-resisting metal is employed in the con-

struction of the plant, whilst the proportion of residual pitch is reduced (*cf.* Section VI., p. 413).

The still-residue, or stearine pitch, is dark, hard, and vitreous in fracture when cold ; it finds an outlet in several directions, such as road-making, tarpaulin material, etc.

This process is not so efficient in many respects as those previously dealt with, but is mainly applicable to fats of low technical value, the acids from which will require distillation in any case to render them fit for technical use.

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SECTION IV.—THE EDIBLE FAT INDUSTRY

Introduction.—The edible fat industry is probably the most important field of application of the natural fatty oils, in respect either to the tonnage of fat handled in the trade annually or to the importance of the industry to civilized life.

Edible fats fall into two main divisions, which, however, overlap to a certain extent :

I. Fats which are consumed as such—butter, margarine, and various fats employed in confectionery.

II. Fats which are used in cookery practice—lard, lard substitutes, and also to a lesser extent butter and margarines.

I. *Edible Fats consumed Uncooked.*—Butter retains its place in popular favour as the preferred fat in this class, and the annual world production of cow's milk butter is certainly well above 1,000,000 tons. To this must be added the production in Asia, Africa, and elsewhere of native butters from the milk of goats, reindeer, buffaloes, etc., statistics for which are unavailable.

At the same time, the production of butter substitutes or margarine has increased very considerably, especially since 1914–1918. During the war of 1914–1918, modern margarine factories in Britain, Holland, and other parts of Western Europe and the United States were constructed or extended on a very large scale.

The nut fats, notably coconut oil, palm kernel oil, and cacao butter with some others, form a more or less separate group because they are used not only in margarine manufacture, but also by themselves in certain cases, especially

in confectionery fats and for some types of biscuit manufacture. The fats used in confectionery form, in fact, a separate problem which has to be considered from various standpoints.

II. *Edible Fats used in Cookery Practice.*—The natural fats lard and suet, especially the former, are the original staple materials of this trade.

The annual world production of lard is probably of the order of 1,000,000 tons, a considerable proportion of which comes from the United States.

In addition, large quantities of lard substitutes, technically known as "lard compounds," are manufactured by blending edible tallow products such as oleostearin with liquid vegetable fats of the cottonseed oil type, or by partial hydrogenation of various liquid fats. Lard and its various substitutes are known as "shortening fats," one of their main uses in cookery being to confer a crisp or flaky nature upon the finished product. The exact type of fat used depends on whether it is to be incorporated in bread, cakes, pastry or biscuits, and of course in certain cases margarine or butter is also employed in addition to lard or lard compounds.

The chapters in this section deal with the ramifications of the edible fat question in approximately the above order, and include references where necessary to the possibility of the introduction of hydrogenated fats into margarine or cooking fats. The section is concluded by brief surveys of the nutritional aspects of the various edible fats and of the problems and nature of rancidity, which is apt to develop in any fat unless certain precautions are observed in its preparation and also in its subsequent storage.

CHAPTER I.—BUTTER

The Physical Nature of Butter.—The production of butter is a manufacture which falls rather within the limits of agricultural chemistry than of ordinary applied chemistry, but it is evident that a fatty material whose yearly consumption runs into many hundred thousand tons is one which demands notice in a work of the present kind.

It should be realized from the outset that butter itself is not simply a fat, but a solid emulsion of water in fat which contains a number of other substances, all of which go to make up the full characteristics of the edible material.

To understand butter technology from a theoretical point of view, it is necessary, then, to have some knowledge of what a solid emulsion is. The theory of emulsions has been the subject of much physico-chemical study in the last few decades, especially in the hands of Pickering, Donnan, Ramsden, Bancroft, Clowes, and others. A fuller description of the theoretical development of the problem than space permits here will be found, for example, in Clayton's *Margarine*, but the present standpoint is briefly as follows.

The emulsions met with in the production of butter and of margarine are primarily cases of two liquid phases, namely, fatty oil and water, any ultimate solid emulsions being due to lowering of the temperature to the point at which the fat is solid.

The cause of permanent emulsification of two liquids is now believed to reside in the presence, in the interfacial layers between the two liquids, of an adsorbed substance. This adsorption layer (*e.g.* of an oil-surface holding a third material adsorbed in the outer film) has the effect of producing a superficial coating on the microscopic globule which in general causes a diminution in interfacial surface tension,

together as a rule with the presence of an electric charge on the globule. Both the surface tension and electrical effects have the result of retarding the agglomeration of the minute particles to form larger ones, *i.e.* for the emulsion to "break" and the liquids to separate into two layers.

If an intimate mixture of a pure liquid fat and water be made by efficient mixing, the resulting emulsion is not permanent and separation into two layers of the practically pure liquids will set in within a comparatively short time; but in presence of small quantities of a suitable colloidal substance (an "emulsifying agent"), soluble in one or both liquids and capable of being concentrated or adsorbed preferentially at the liquid interface, stable emulsions can be produced. In the case of an emulsifying agent which is soluble in both liquids it is possible to produce, for example, either emulsions of liquid fat in water or of water in liquid fat. In the first instance the droplets of liquid fat are suspended in a continuous phase of water, and in the second the reverse holds and the liquid fat is the continuous phase.

Milk is an emulsion of butter fat in water maintained by casein or other colloid which is soluble in either medium; on the contrary, butter is an emulsion of water in butter fat. The procedure of butter manufacture is, to the physical chemist, the interchange of the "continuous" (water) and "disperse" (fat) phases originally present in the milk.

The Modern Production of Cow's Butter.—It is needless to dwell on the fact that, as has happened in other industries, technical practice forestalled the physico-chemical explanation of the process of butter-making by many centuries; as a matter of fact, the investigation of colloidal emulsification from a theoretical standpoint is by no means easy, and it is only of recent years that the matter has become somewhat clearer to understand.

Of course, farm or *dairy butter*, as it is now termed, has been made from time immemorial in individual farms by churning the milk or cream and subsequently separating the product and kneading or beating it by hand.

The principles of butter manufacture have remained unaltered and modern practice only varies in the improved mechanical methods and hygiene which obtain, together with the assistance of certain biochemical adjuncts.

The original fat-in-water emulsion, milk, separates on standing into two similar emulsions differing mainly in relative composition : the upper layer of cream contains much more fat than the lower layer of skim-milk. Whole milk contains about 3·6 per cent. of fat, and cream as a rule from 35 to 45 per cent. of fat.

In most of the small farm dairies the cream would be skimmed off the milk rather than the whole milk churned ; in either case the action of churning is to "break" the fat-in-water emulsion and to produce, not simply fat and water, but two distinct liquids : (a) buttermilk, which is an aqueous solution of milk colloids, including casein and other materials, and (b) butter, which is a new emulsion of water-in-fat. To render the latter coherent and non-watery it would be kneaded or beaten, this process forcing out the residual buttermilk which remained entangled between the globules of water-in-fat emulsion.

In addition to the obvious advantages of churning the cream rather than the whole milk, the small butter producers of olden times soon noticed that fresh cream was more difficult to churn than cream which had "ripened," i.e. in which a gentle acidic fermentation had commenced, and they introduced the practice of churning cream to which some buttermilk from a previous batch had been added.

The modern practice is simply a development of these ideas, and modern *creamery butter*, as it is called, is made in large dairies to which milk from various herds, possibly over a large area, is conveyed. Great attention is paid to the hygienic aspect of butter production, not only in the cleanliness of the plant and apparatus employed, but with regard to the control of the bacterial and enzyme contents of the milk. The milk is separated centrifugally into cream, and the latter, as a rule, is pasteurized (i.e. partially

sterilized) and then inoculated with a lactic acid ferment and soured to a point which renders the butter-making process easy, without, however, producing an acidity which will coagulate the casein present. The soured or ripened cream is then churned mechanically at about the ordinary temperature, and the resulting butter is passed through machine rolls in order to "knead" it and press out the retained buttermilk.

In America a third variety of butter, "*factory butter*," is marketed to some extent. This consists of poor quality or stale butters, which are melted and the butter fat extracted in a centrifugal separator. The recovered butter fat is washed and then aerated by a stream of cool air, after which it is mixed with soured milk, emulsified, chilled rapidly, and rolled. It is then indistinguishable in chemical and most physical characteristics from fresh butter.

Some Characteristic Features of Dairy Butter.—

(i) *Vitamin content*.—Butter is a good source of vitamin A and, to a less but still definite degree, of vitamin D. The assay of these vitamins in butter has been the subject of much investigation, the details of which are given in communications to scientific journals and summarized in reports such as the American *Annual Reports of Biochemistry*. Briefly, these assays are either biological or chemical. For vitamin D the biological technique is essential, for vitamin A it may be paralleled satisfactorily by the more rapid chemical examination. The latter is best effected by careful extraction of the "unsaponifiable matter" of the butter (including vitamin A), and submitting it either to spectrographic analysis, when the intensity of the characteristic absorption band of vitamin A at $328m\mu$ is determined, or forming the characteristic blue-coloured compound with antimony trichloride in chloroform solution and similarly determining the intensities of its characteristic absorption bands at 606 and $572m\mu$.

The vitamin A of butter is derived from β -carotene assimilated from the pasture diet of the cow and therefore, normally, summer butters from cattle feeding almost

entirely on fresh grass contain definitely more vitamin A than winter butters. The latter can, however, be made more equivalent to summer butter in this respect if carotene is present in the feed (grass silage dried so as to preserve the carotenoids present) or if vitamin A is added to the diet (inclusion of suitable fats which themselves contain it or carotene). The vitamin-A content of butter has also been shown to depend to some extent on other conditions, and it may vary in different breeds of cow.

(ii) *Flavour or "aroma."*—The full flavour of dairy butter is one of its features most difficult to reproduce in margarine. The source of the very characteristic butter "aroma" has been much discussed and agreement has not yet been finally reached. It was formerly considered to be due to the glycerides of lower saturated acids present—"tributyrin." But it is now known that this particular glyceride is not present in butter fat and that butyric and the other acids of low molecular weight are mainly present only once in any triglyceride molecule, the other acyl radicals being usually either those of oleic or palmitic acids. In some relatively small proportion of the triglyceride molecules, there will be two butyric groups with one oleic or palmitic group. The molecular weight of any of the triglycerides present is thus quite large and it is extremely unlikely that any of them will possess any definite flavour, any more than the more common mixed glycerides (such as the palmito-oleins) which are completely tasteless.

The characteristic flavour more probably resides in minor non-glyceridic components present in minute amounts in the butter. It has been suggested that traces of phosphatides ("lecithin") or of milk casein may be responsible, and these may be admitted as possible factors. Definite evidence has, however, been given that natural butter contains traces of acetyl methyl carbinol, $\text{CH}_3.\text{CO}.\text{CH}(\text{OH}).\text{CH}_3$, probably produced as a by-product of the acid fermentation in the "ripening" of the cream. Acetyl methyl carbinol is practically tasteless, but is readily oxidized to diacetyl, $\text{CH}_3.\text{CO}.\text{CO}.\text{CH}_3$, and it is generally accepted at present that

much of the flavour of butter is due to the presence of traces (0.3–2.0 parts per million) of this diketone.

(iii) *Consistency*.—Another feature of butter which is very difficult to reproduce completely in its substitute margarine is what is usually referred to as "spreadability," a term which is self-descriptive. It is easy to produce mixtures of other fats of the same "melting point," or rather range of melting, as butter fat, and to convert these into emulsions the physical properties of which are very close to those of butter, except that the ease of spreading on a surface (*e.g.* bread) is much more difficult to attain.

This characteristic of butter is doubtless definitely dependent on its glyceride structure and on the presence of the lower saturated fatty acids linked as mixed glycerides with the more usual type of higher fatty acids. Not only is it difficult or impossible to simulate exactly the mixture of mixed glycerides which is butter fat by physical blending of fats of different composition, but it may be guessed that some at least of the special spreading properties of butter are due to those glycerides which contain both very short (butyric) and long chain acyl groups combined in the same triglyceride molecule.

(iv) *Storage*.—From its mode of preparation, and the enzymes present in the cream, butter is peculiarly liable to deteriorate owing to the onset of rancidity. Various manifestations of rancidity may occur, of which the hydrolytic types, or the more drastic oxidative types, either of which may lead to the production of free acids of low molecular weight, are least troublesome. Extreme rancidity due to presence of free lower fatty acids is comparatively rare. The more usual trouble is the development of somewhat stale flavours, termed "tallowy" or "off" flavours, which result from slight oxidative changes. The chemical changes involved in oxidative rancidity are considered in a later chapter (p. 324) and here it is only necessary to indicate the special precautions desirable in regard to butter. The problem is not acute in home-produced butters, but much of the supplies to this country come, of course, from

Australia and New Zealand. It is now generally recognized that storage at low temperatures (0° to -10°) during transport and warehousing is an important aid to retarding the development of off flavours, whilst in addition it is desirable to wrap the butter in packages which are impervious to light and air. Barnicoat goes so far as to state that the only completely satisfactory wrapper for prolonged storage is metal foil waxed on to parchment paper. Maintenance of a cool atmosphere and dim light during processing and packing of the butter is also important.

Ghee (Indian, Egyptian) Butter.—A note may be added here that in several Eastern countries the milk of cows, buffaloes or goats is churned (sometimes in a goat's skin) until butter forms. The product is heated until considerable separation of butter fat occurs, and the fat is poured off and used as butter by the natives. By this process considerable acidity may be introduced into the fat, which may possess a rancid taste and sour odour which are usually by no means pleasant to Western ideas ; on the other hand, the best quality ghees are pale-coloured fats with a fresh, butter-like odour. The production of ghee and similar butters in Asia and some parts of Africa is sufficiently great, in comparison with that of cow's butter in the rest of the world, to warrant reference.

Standards of Analysis of Butter.—Butter analysis is, of course, a very large subject and its technical literature is correspondingly abundant. It is only necessary here to state that the maximum amount of water permitted in butter in Britain is 16 per cent., and that an average good butter contains :

								Per cent.
Fat	85
Curd (casein, etc.)	1
Salt	1
Water	13

The main points of butter analysis are as follows :

- (a) Determination of water, salt, "total solids not fat," and total fat ;
- (b) Tests for the presence of preservatives such as boric

or benzoic acids and colouring matters (natural or aniline dyes) ;

(c) Examination of the fat.

(d) Examination of the vitamin A and D contents.

As regards the fat, the chief assistance is derived from the refractive index and especially from the Reichert-Meissl value, which indicates the proportion of water-soluble fatty acids volatile in steam (*cf.* Section I., Chapter IV., pp. 55-59) and which should be about 25-30 in the case of true butter. On the other hand, the Polenske value (water-insoluble volatile fatty acids) should not exceed 3, a higher figure indicating the presence of excessive amounts of capric and lauric acids, *i.e.* the probable addition of a nut fat such as palm kernel or coconut oil. The Reichert-Meissl value of true butter is much higher than that of any substitute at present known on account of the characteristic amount of butyric (and to a less extent, caproic and caprylic) acid combined in the fat. This renders the Reichert-Meissl value practically conclusive as a test for butter, pending any synthetic introduction of butyric acid into vegetable butters as has been suggested in some recent patents (*cf.* p. 305).

The analytical methods referred to will be found in Section I., Chapter IV., pp. 56, 57, and a discussion of the chemical composition of butter fat in Section II., Chapter III., pp. 167-170. The vitamin assay of butter and other fats has been briefly mentioned in a preceding paragraph (p. 288).

Cheese.—The manufacture of cheese is as highly technical a process as that of butter, but except in so far as it contains from 30 to 40 per cent. of fat as usually prepared (or from about 45 to 55 per cent. on the dry material), its connection with fat technology is much more remote than in the case of butter. The specific properties of cheeses, that is to say, depend entirely on the fermentation processes involved and the products of fermentation which characterize various kinds of cheese are not closely connected with their fat-content. Whilst, therefore, the technology of cheese-making forms a highly instructive chapter in applied biochemistry, it is not possible to discuss it further here.

The fats present in cheese are, when the latter has been prepared from whole milk, those present in the original cream, *i.e.* butter fat. In some makes of cheese, skimmed milk is used as the raw material, and in these instances fat of the premier jus or oleo oil type may be added to compensate for the deficiency in butter fat. This is detected by observation of the Reichert-Meissl and Polenske values of the cheese fat, and analysis of the cheese fat is indeed resorted to in order to determine whether the cheese has been prepared from whole or skim milk.

CHAPTER II.—MARGARINE (BUTTER SUBSTITUTES)

The Development of the Margarine Industry.—The partial replacement of butter and lard by other fats dates only from about 1870, the industry having grown in the meantime to vast proportions. Like the soda-ash and some other industries, the process had its origin in France and was stimulated by war conditions : the French Government offered a prize for a successful butter substitute at the time of the Franco-German War of 1870, and Mège-Mouriès brought forward a process by which he believed it was possible to transform beef fat into butter by digestion with a mild alkaline solution in presence of the natural gastric and pancreatic juices of pigs' or sheep's stomachs.

The somewhat crude, partially fermented fat so obtained was butter-like in appearance and flavour, and the production of margarine, as it was termed, spread fairly rapidly to other countries. During the first twenty or thirty years of its manufacture, however, margarine was an article which was, frankly, a butter substitute of a somewhat inferior type, and the good points of the commodity were overclouded by production of a certain proportion of cheap, inferior, and sometimes non-hygienic fat under this name for edible purposes by small traders. From about the commencement of the present century, however, the manufacture of fats other than butter of the highest quality, not only as butter substitutes, but for confectionery and all types of cooking fat, began to be handled seriously by large manufacturing concerns, and the war of 1914–1918 probably helped to remove from public opinion the prejudices which remained (and which at one time had some justification) against the use of “artificial butter.”

The original methods of the first margarine makers had in the meantime been developed and revised ; so much so, that modern margarine is essentially different in many respects from that of 1870.

The butter consistency and flavour, originally obtained by a partial fermentative action on beef fat, are now secured by producing an emulsion of pure animal and/or vegetable fat with milk which has been " soured " slightly by controlled enzymic action ; the fats employed include not only the highest qualities of beef fat or lard, but also many highly refined vegetable fats of suitable consistency, together with, in some cases, partially hydrogenated high-grade fats of diverse origin ; and, whilst every attention is now paid to carrying on the processes of manufacture under the most hygienic conditions, the aid of mechanical engineering and of the physical chemistry of emulsions is sought in order to produce products which completely simulate in physical properties the natural butter or lard, and approximate to them in the nature of their actual ingredients.

In the present chapter we are concerned with the wide variety of products which replace butter, whether employed in its original state or in culinary operations such as cake, biscuit, or pastry making, and the main principles which are utilized in their manufacture at the present time.

The general scheme of production of margarine as a butter substitute is as follows :

1. (a) Selection and preparation of the fats to be incorporated ;
(b) Partial sterilization (pasteurization) and inoculation (" souring ") of the milk employed.
2. Emulsification of the prepared fat with the prepared milk.
3. Chilling, kneading, and rolling of the product to produce the physical appearance of butter.
4. Incorporation of salt, colouring, or caramelizing substances.

Selection of Fats for Use in Margarine.—The formulæ used in proportioning the fats for butter substitutes

are very large in number, and are to a certain extent regarded as trade secrets by makers of the various brands. They are mainly determined, however, by the following considerations :—

1. The desired melting point of the mixture of fats, which is about 24–26° C. for butter substitutes (either for table purposes or as baking or "cake" margarine), and about 37° or even higher for pastry and "shortening" fats (which are, however, more of the nature of lard substitutes and will be considered with the latter in Chapter V. of this section).

2. The type of margarine, *i.e.*, whether "animal fat margarine" in which animal fats preponderate, or "vegetable margarine" in which the animal fats do not exceed about 20 per cent.

3. The season of production—margarine for table purposes is made somewhat harder from early summer onwards until late autumn. It should be pointed out that the modern margarine trade is so organized that the supply is fairly rapidly disposed of, and it is probably exceptional for the commodity as retailed to have been produced for much more than six weeks—about two or three weeks between manufacture and consumption is probably an average time.

4. The current market values of the various oils which are available for use in margarine.

Some idea of the formulæ employed in margarine fat-blending may be gathered from specifications which were recommended in this country in the latter stages of the war of 1914–1918 by the Food Investigation Board :

—	Animal fat margarine.	Vegetable fat margarine.		Baking margarine.	Pastry margarine.
		May.	November.		
Premier jus ..	10	15	20	—	20
Oleo oil ..	30	—	—	—	—
Oleostearin ..	—	—	—	—	35
Neutral lard ..	15	—	—	—	—
Palmkernel oil ..	—	50	50	10	35
Coconut oil ..	20	15	—	70	—
Cottonseed oil ..	25	10	20	20	10
Groundnut oil ..	—	10	10	—	—

The various fats which are most frequently used in margarines are obtained from the following sources :

Animal Fats.—The most commonly employed constituents are *premier jus* from the best parts of cattle, and the corresponding *oleo oil* which is produced on expressing the latter (*cf.* pp. 138, 214); *lard* of the grades *neutral No. 1* and *neutral No. 2* is also used to some extent, and occasionally *oleostearin*, the latter to counterbalance the presence of larger proportions than usual of liquid vegetable fats.

Vegetable Fats.—The chief of these, for the present purpose, are coconut and palm kernel oils, groundnut and cottonseed oils. Other oils which are coming forward as suitable constituents or additions to these include refined palm oil, soya bean, sunflower seed, rape and sesame oils.

In somewhat lower grades of margarine, quite suitable for cooking purposes, the liquid oils may be partially or entirely replaced by kapok, maize, and one or two other liquid fats. It is to be anticipated that the solid or semi-solid vegetable fats, now represented only by palm kernel, coconut, and palm oils, will be added to as time goes on by the employment of babassu, cohune, and other tropical nut fats and by tropical nut butters, such as shea and mowrah butters.

Hydrogenated Fats.—Several liquid fats are convertible by hydrogenation into semi-solid fats suitable for margarine. It is desirable to pursue hydrogenation to a stage at which but little polyethenoid unsaturation remains and where necessary the products may be made harder than is required for margarine and then blended with soft or liquid fats to attain the required consistency.

Whale oil is probably the most important source of hydrogenated fat for margarine. There has been considerable prejudice in this country against its use, although on the Continent hydrogenated whale oil has been a normal component of margarine for many years. Since raw No. 1 grade whale oil, produced in modern factory ships, is one of the cleanest crude fatty oils available technically, and is

superior in colour and free acidity to many of the corresponding raw vegetable fatty oils destined for use in margarine, there can be no valid objection to its use on hygienic grounds. The only point to be seriously considered is the presence of some glycerides of highly unsaturated C₂₀ and C₂₂ acids in whale oil. On account of ease of oxidation, these should be converted as far as possible to mono-ethenoid or saturated glycerides, which involves hydrogenation of the whole fat to a fairly low iodine value (30–45) because the complete reduction of these particular components is not a rapid process (*cf.* Section III., Chapter III, p. 261). However, hydrogenated whale oils of iodine values of about 65–75 can be utilized fairly well, by suitable blending and for use in margarines which have not to be stored for long before use.

The objection to hardened fats for edible uses on the score of possible presence of traces of nickel would apply to other hydrogenated fats as well as whale oil, but it has been shown to be groundless (*cf.* p. 321). Other (vegetable) fatty oils which are, indeed, hydrogenated on an extensive scale for margarine or for cooking fats include groundnut, cotton-seed, soya bean and, to a less extent, sunflower seed and rape oils.

The characteristic properties, occurrence, and extraction of all the foregoing materials have been described in Section II., Chapters II. and III., and Section III., Chapter I. The vitamin or accessory growth factor problem is discussed in Chapter VI. of this section, but it may be said here that of all the above fats, those from beef (premier jus, oleo oil, and oleostearin) are the only ones in which the fat-soluble vitamins can be carried through to margarine: they are said to be absent from lard and almost certainly do not survive the processes of refining (or hydrogenation) applied to all the vegetable oils and to whale oil.

Fats for use in margarine manufacture must be colourless, odourless, neutral, and free from taste (other than perhaps a very faint nutty flavour); their preparation therefore consists in refining and deodorization, with any necessary

neutralization of free acidity, as described in Section III., Chapter II., with the following reservations :

(a) The animal fats used—*premier jus*, *oleo oil*, *oleostearin*, and *lards*—are of such a degree of purity when rendered that further refining is unnecessary; the free acidity of the best qualities of these products does not exceed 0·25 per cent. as *oleic acid*. It therefore becomes possible to preserve any vitamins present in beef fat and the natural pleasant flavour of the fresh animal fat.

(b) The vegetable fats used contain in the raw state, as a rule, more free fatty acid than can be tolerated in the finished margarine, and also, frequently, are somewhat more coloured than is desired, in addition to possessing slight characteristic odours which are undesired.

Coconut and palm kernel oils as used in edible fats are usually of a very fair colour in the raw condition, and their refining consists in removing the free fatty acid present (usually 3–5 per cent.) by neutralization with soda, as described on p. 231. In preparing any vegetable fat for edible purposes it is well to wash the neutralized oil with a very dilute solution of sodium carbonate in order to remove the last traces of free fatty acid—the finished neutral fat should not contain above 0·1 per cent. of free acidity. The alkali-washed fat is then very thoroughly washed with water to remove the last traces of soap, and the oils are then further refined, as a rule, by agitation with fuller's earth or adsorbent charcoal.

The reddish colour of palm oil is removed, before or after neutralization of the free fatty acid, by agitation with activated fuller's earth (*cf.* p. 224). The bleached palm oil is a cream, almost white fat in the solid state and clear golden yellow when melted.

Cottonseed oil is refined mainly in the course of neutralization of the free fatty acids as described on p. 233, the somewhat intense yellow flavonic colouring matters of the oil being removed by alkali at the same time as free fatty acid. Fuller's earth bleaching is also frequently employed subsequently to neutralization, and the same

sequence of operations is generally adopted in the case of groundnut, maize, soya bean, sunflower, rape, and other vegetable fats which are also used in various parts of the world. The exact procedure adopted is governed, of course, by the colour and specific nature of the raw oil handled.

Whatever the oil, it is finally subjected to the process of deodorization under high vacuum at an elevated temperature, as described on p. 237, in order to eliminate all traces of the odiferous or flavouring non-fatty principles which have found their way into the crude oil during the original extraction of the seed, and it is then ready for blending with other fats to produce the desired mixture which is the fatty basis of the margarine.

(c) Hydrogenated fats for edible purposes are usually neutralized and earthed prior to hydrogenation. During the latter process the colour is usually further improved, but slight increase in free acidity may occur and a characteristic aroma known as "hardening flavour" is liable to develop. The hydrogenated fats are therefore preferably again neutralized and washed and then carefully deodorized as for vegetable fats (*v. supra*). "Hardening flavour," however, is a term covering more than one factor; for instance, traces of ketonic or other by-products which are removed once for all by deodorization, but also another factor which may "revert" or redevelop when the completely odourless and tasteless deodorized fat has been stored for some time. This tendency to reversion is less, and ultimately disappears, when hydrogenation has been continued until a fairly hard fat has been produced. It is probably caused by slight oxidative changes in some of the semi-hydrogenated fat (probably components still possessing polyethenoid unsaturation), and no real remedy except hydrogenation to a fat of higher melting point than is primarily requisite for margarine has been discovered. In conformity with the explanation offered, it is noticeable that this factor is more troublesome in hardened whale oil than in most of the hydrogenated vegetable fats.

Selection and Preparation of Milk for Use in

Margarine.—The milk employed is, in the best factories, derived from known sources of a high degree of purity and as fresh as possible. It will be borne in mind that the addition of milk serves a double purpose :

- (i) To emulsify the fat and produce a physical consistence similar to butter ;
- (ii) To introduce a flavour into the finished margarine which resembles that of butter as closely as possible. This is effected by allowing the milk to undergo to some extent a lactic acid fermentation under controlled conditions : the milk is first of all "pasteurized" by passage through an apparatus, usually continuous, in which it is maintained at a temperature of 60–65° C. for half an hour. The ferment employed is a pure culture of *Bacillus lactis acidi*, usually supplied as a powder made by mixing the pure culture with lactose, starch, or similar inert material and drying under vacuum at a low temperature. About 1½ ounces of this "starter," as it is termed technically, are added to 3–4 quarts of pasteurized milk which is maintained at 30–35° C., a temperature at which the organism very rapidly grows and produces lactic acid, furnishing a medium which is unfavourable to the growth of any undesired foreign bacilli which may also be present. After about 18 hours an abundant soft curd will have formed and the developed "mother-starter," as this liquor is called, is rapidly cooled to 0° C. and maintained at that temperature to curtail further growth. More of the pasteurized milk is then inoculated with about 3–6 per cent. of the mother-starter and fermented or "ripened" at 18° C. for about 18 hours, the lower temperature being employed in the main fermentation because the flavour and aroma of the final product is more perfect than at the temperature of most rapid development of the lactic acid organism. This product can now be used in margarine manufacture, but is usually employed as an intermediate culture to inoculate still larger quantities of pasteurized milk, which is likewise "ripened" at 18° C. for about 18 hours and then employed to emulsify the prepared fat.

Needless to say, the whole of the process of "ripening" or "souring" demands constant routine control to ensure on the one hand the most desirable flavour and aroma, and on the other to guard against the introduction or growth of other types of bacilli or moulds.

Emulsification of the Prepared Fat with the Prepared Milk, and subsequent Chilling, Treating, and Rolling.—The fat and milk have now to be intimately mixed at a slightly elevated temperature into the most perfect emulsion possible, which must then be chilled rapidly so as to stabilize it permanently by solidification. Small amounts of special agents, *e.g.* "Palsgaard emulsion oil" (an air-blown soya bean oil), or of monoglycerides ($C_3H_5(OH)_2O.CO.R$), are sometimes added to promote emulsification.

The actual emulsification of fat and milk is carried out by one of two methods—a "batch" or a continuous process. The batch process was the first in operation, but later this seemed likely to be superseded by a continuously operating emulsifying machine. Present practice in this country, however, seems on the whole to have reverted to the older principle in many of the larger factories.

The discontinuous process is carried out in specially designed churning vessels, which make batches of about 1 ton of emulsion at a time, the melted fat being run into the "ripened" milk with vigorous agitation at about 40° C. The quantity of milk employed is such that there will be about 16–25 per cent. of water in the emulsion. The contents of the churn are finally cooled, whilst agitation continues, to about 25° C. and then run off and caused to meet a spray of ice-cold pure water, whereby it is chilled and collected from the adherent water in a cooling trough, or more usually, in modern factories, as described below.

In the continuous plants, any given portion of fat and milk is only churned for a very short time, but the texture of the emulsion produced is evidently considered by many authorities to be less satisfactory than that obtained in the large churning vessels discussed in the preceding paragraph. Emulsi-

fication by the continuous method may be carried out in a jacketed cylinder maintained at 25–35° C., the cylinder carrying a horizontal stirrer shaft fitted with blades working against perforated baffle plates fixed on the circumference of the cylinder, the perforations becoming more minute as the emulsion travels towards the exit. The shaft is rotated at about 1,500 r.p.m. and the fats and prepared milk are fed into the cylinder at accurately proportioned rates of flow. A continuous unit of this type will produce several tons of margarine per hour with a lower expenditure of power than the batch emulsifiers, but, as stated, the latter type of plant has other advantages and is frequently preferred.

The emulsion produced, instead of being chilled by direct contact with water, is now more frequently fed into a trough into which dips a comparatively narrow rotating cylinder warmed internally by water at about 35° C. Another cylinder of much larger diameter, and cooled internally by refrigerated calcium chloride solution at about –7 to –10° C., is placed so that it is in contact with the smaller drum and rotates in the same direction. By suitably adjusting the rates of rotation of each drum the liquid emulsion is picked up by the smaller drum and transferred to the larger cooling drum, where it is retained for a considerable proportion of a revolution before being removed in the solid state by a fixed horizontal knife or scraper.

The chilled emulsion now falls into a collecting trough fitted with a rotating Archimedean screw-gear which propels it forward to the rolling machinery, which consists most frequently of large revolving drums fitted with internal rollers. The action of these is mechanically to knead and press the solidified emulsion together so that it forms a coherent mass which will not retain more than the legally permissible limit of 16 per cent. of moisture. In most cases a moisture content of about 13 per cent. is aimed at.

Incorporation in Margarine of Vitamins A and D, Salt, Colouring, or Caramelizing Substances.—The margarine is now complete as regards its consistency and

general composition, but other components may have been introduced either at the emulsification stage or in the subsequent kneading process.

The most important of these additions to margarine is undoubtedly that of vitamins A and D concentrates. This advance, dating from about 1928, was first made in the Bromborough, Cheshire, factory of Planters Foods, Ltd. (an associated company of Lever Brothers, Ltd.), and the production of "vitaminized margarines" with vitamin A and D contents equal to those of best summer dairy butter has since become an accepted feature of the trade. Such margarines may be considered in every respect the nutritive equivalents of the best butters. The source of the vitamins is usually whale liver, less frequently cod or similar fish livers. The unsaponifiable fractions of the liver oils are separated and contain, of course, the vitamins present in the oils in a concentrated form. The concentrates are introduced into the margarine during the processes of emulsification.

Other additions may include salt or colouring matters, such as minute proportions of a yellow coal-tar dyestuff, with a view to simulating still further the usual taste and appearance of butter. Although public taste may demand such additions, it is obvious that they are in actuality neither an improvement nor a detriment to the product.

The similar addition of small quantities of carbohydrate or protein products such as dried milk, egg-albumen, or glucose is, however, more useful in that it confers on margarine the properties of browning and frothing when heated which are definitely desirable in some cases in cookery, and which the original margarine, contrary to butter, does not possess.

Any or all of these additions are made by mixing the rolled margarine in a blender machine (a dry mixing mill) with the necessary but small proportions of one or other of the foregoing materials.

If a "preservative" such as boric acid or the like is to be added, it is also introduced at this stage, but the use of

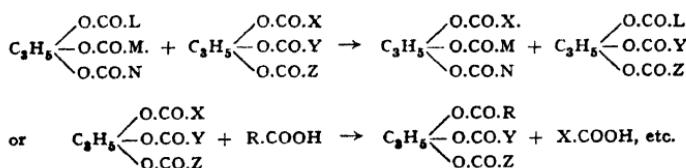
preservatives other than salt in margarine should be unnecessary and is to be deprecated.

As regards the packing of the finished product, it is obvious that this should be as mechanical as possible and that precautions are equally necessary at this point, as in the general preparation, to ensure that the product, which in its best modern forms is entirely pure and hygienic, should not be exposed to the slightest contamination by bacterial organisms or moulds.

Alteration of Consistency of Margarine Fats by "Interestericification" Processes.—As stated on p. 290, it is not easy to reproduce in margarine the characteristic "spreadability" of butter. Much depends on the choice of the fats which are blended into the margarine, and in practice this selection is made so as to result in a final product the consistency of which approaches that of natural butter as nearly as possible, and the matter is left at that.

Suggestions have, however, been made, and processes patented, with the objects either of interchanging the acyl radicals between the triglyceride molecules of the mixture of fats used, or of introducing a certain amount of butyro-glycerides into the margarine fats. Brief reference may be made to these "interestericification" processes, as they have been termed, although it is doubtful whether they have yet found technical application.

It has been found that, when a mixture of triglycerides, or of triglycerides and free fatty acids, is heated at about or above 250° in presence of a variety of catalysts, interchanges occur of the general types :

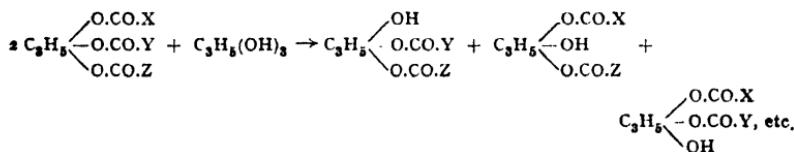


The metal tin, its oxides and some of its salts, appear to be the most efficient promoters of interestericification, but metallic soaps of the higher fatty acids are also effective

and, in lesser degree, a number of other metallic oxides and salts, including siliceous materials such as clays, fuller's earths, and diatomaceous earths. Suggestions are made, in the patents concerned, in the following directions :—

- (i) To employ the process on a mixture of fats in order to induce rearrangement of the mixed glycerides present and to form new types of mixed glycerides not present in the original fats ;
- (ii) To submit a mixture of fats and butyric acid to the process, whereby a certain amount of mixed butyro-glycerides are produced with liberation of a corresponding quantity of higher fatty acids.

In another direction, the same procedure is applicable to mixtures of mixed glycerides and glycerol. When these are treated in the manner indicated above, some proportion of mono- and di-glycerides is produced in the fat, *e.g.* :



The presence of small proportions of mono- or di-glycerides assists the emulsifying properties of fats, and the addition of these compounds is sometimes recommended and practised for this reason (*cf.* p. 302). It should be repeated, however, that the use of interesterification processes as described above has not yet, so far as is known, developed to any extent on the practical scale.

CHAPTER III.—THE VEGETABLE OR NUT BUTTERS

IN contradistinction to margarine fat, which, as we have seen, is a blend of various vegetable and/or animal fats, certain of the tropical nut fats find a certain application for edible purposes in the unmixed condition, and a short chapter is therefore interpolated to indicate which of these are found on the market in the unblended state at present and the chief ends which they serve.

In the first place, it may be noted that the process of conversion of such fats to the edible state is that previously indicated for the vegetable fats used in margarine : crude fat of the highest grade only, both as regards low free acidity and absence of staleness or rancidity, is employed for edible purposes, and the fats are neutralized, washed completely free from soap, bleached by adsorbent earths or charcoal, and finally deodorized at high temperature and under as high a vacuum as possible before being cooled under vacuum and run into enamelled moulds or racked off into large containers.

The fats which find most use in the unblended state are those which possess some specific physical characteristic, especially that of combining a melting point not exceeding about 38° C. with a hard, relatively non-greasy and brittle consistency in the solid state. Fats or "vegetable butters" which possess this "snap," to use the technical term, are valued both for chocolate and other forms of confectionery and also in biscuit-making.

The chief species at present on the market, and their main applications in the edible trade, are as follows :

Refined deodorized *coconut oil* and *palm kernel oil* are

solid fats, colourless, odourless, and tasteless, which melt at about 23–28° C. They find considerable use as an admixture in chocolate and confectionery fats, and have also found favour with strict vegetarians as a pleasant substitute for butter or margarine. The sensation of melting coconut or palm kernel oil on the palate, although quite distinct from that of butter, is very pleasing and in no way greasy.

These fats are, of course, also used very largely in the blended state in margarines, as indicated in the preceding chapter.

Refined and deodorized *babassu* or *murumuru* fats are commodities which are beginning to find similar applications to coconut and palm kernel oils.

It should be noted that coconut and palm kernel oils, the iodine values of which are respectively only 8–10 and 15–20, are converted by hydrogenation into saturated fats which melt at about 41° C. (*i.e.* little higher than the original fats) whilst the brittle consistency of the hardened product is much more marked than that of the original fat.

Coconut oil, and to a less extent palm kernel oil, are technically separated into "stearins" and "oleins" by passing through filter presses, similarly to the production of beef stearin and oleo oil from premier jus (p. 138). Coconut "stearin," the more solid or higher-melting portion of coconut oil, contains large proportions of dilauromyristin and closely related mixed glycerides. In consequence it has a melting point and a certain degree of brittleness which make it serviceable as a substitute for cacao butter in chocolate fats, and it has found considerable use for this purpose.

Cacao butter generally comes on the market in the refined, but not bleached and deodorized, state, the colour, odour, and flavour not being detrimental in any way to its employment in confectionery. Its main use is in chocolate-making and other forms of confectionery, for which it commands a fairly high price, its substitution by one or other of the foregoing fats being thus encouraged.

Refined and deodorized *Borneo tallow* (*cf.* p. 116) is a slightly greenish fat of similar melting point to cacao butter, with an almost equal degree of brittleness and "snap." It is used increasingly, and practically exclusively, as an excellent substitute for cacao butter in chocolate and confectionery.

Refined, deodorized *palm oil* is now produced in quantity for edible purposes and forms an almost colourless, somewhat dull-looking soft fat which is pleasant to the palate and finds increasing use with bakers and biscuit manufacturers, whilst it is also blended as a component of margarine by some makers. In this case, again, there would appear to be scope for the utilization of a refined deodorized, partly hydrogenated palm oil of melting point not exceeding 40° C., but it is somewhat doubtful, in view of the composition of palm oil (*cf.* pp. 159, 161), whether anything of a brittle texture can be anticipated in the case of this fat.

This chapter may be fittingly concluded by repeating the reminder already given that many sources of tropical vegetable butter fats probably remain untapped or but little developed, and that further substitutes for the above oils are seemingly available in abundance as follows :

Coconut, palm kernel, and cacao butter (brittle fat) types : Cohune oil and other fats of the *Attalea*, *Allanblackia*, *Shorea*, etc., genera of South and Central America, West Africa, and the East Indies; Chinese vegetable tallow, nutmeg, or other fats of the *Myristicaceæ*.

Palm oil (soft fat) types : Illipé butter (Bassia fat); mowrah butter; shea butter.

CHAPTER IV.—CONFECTIONERY FATS

THE chief use of fats in confectionery is in connection with chocolate, toffee, and caramels, and the qualities required are digestibility equal to that of ordinary butter combined with a physical texture which is not greasy, is hard and "snappy" or brittle (whilst the melting point is not above 37–38° C.), and which is permanently bright and clear at the surface.

Very few natural fats possess all these properties at the same time, the most perfect materials for the purpose being cacao butter, Borneo tallow, *Allanblackia* and *Garcinia* fats, probably in the order given.

The fats in question all melt near 30° C., and yet are quite hard and brittle when cold. This is commonly attributed, and no doubt correctly, to the presence of a simpler mixture of constituent glycerides than is found in most other oils, e.g. coconut or palm kernel oils. The component fatty acids in each case are almost wholly oleic, palmitic, and stearic, and these fats contain much oleopalmitostearin, oleodistearin, or oleodipalmitin, the greater part of the oleic acid being combined with two saturated fatty acid residues in the glyceride molecules. The mixture of mixed glycerides present in the fats mentioned is thus much simpler than in the nut oils or in other fats of butter, lard, or tallow consistency, and it is this factor which renders them physically most suitable for use in confectionery.

As indicated in the last chapter, however, it is possible to obtain more or less satisfactory substitutes for these fats, which are somewhat expensive, by employing babassu or murumuru fat or hardened coconut or palm kernel oils. Furthermore, the addition of a certain proportion of edible

coconut or palm kernel oil or "stearin" to cacao butter is sometimes practised for chocolate fats.

An important problem in the application of any fat in chocolate or caramels is what is known as "fat-bloom." Many of the fats used, and all of them if care is not exercised in the cooling of the finished confectionery, are liable to give rise on keeping to a misty appearance on the surface somewhat similar to the "bloom" on certain kinds of fruit. This is undesirable in chocolates, etc., because it spoils the bright clear appearance of the confectionery; and considerable work has been carried out to determine the cause of fat-bloom and to devise means for avoiding it. The phenomenon is liable to occur even with cacao butter as the fatty medium, and it is now definitely assigned to the separation and crystallization, apart from the mass itself or after the butter has become practically set, of small quantities of fat crystals composed of the highest-melting individual glycerides present in the fat. This separation is most liable to occur at certain temperatures, which depend upon the specific capacity of the glycerides concerned to crystallize in stable forms at those temperatures.

No complete remedy has yet been found: removal of the higher melting fractions by expression at a suitable temperature would be too wasteful and costly a procedure, and would moreover defeat its own ends, because the residual fat would then be of a softer texture than is desirable. It has been found that prolonged working of the chocolate mixture ("conching") prior to its setting reduces the tendency to "bloom," whilst the addition of certain emulsifying agents, notably lecithin, has been recommended for the purpose. It has recently been found that incorporation with the chocolate mixture of about 0.5 per cent. of cacao butter which has been blown with air at 250° for a prolonged period has the effect of greatly reducing the tendency to "bloom." The influence of such additions probably resides in a dispersing effect on the molecular aggregates of the fat, with the result that any crystals which eventually separate at or near the surface of the chocolate are very much more

minute (and therefore less visible as "bloom") than in the absence of the emulsifying or dispersing agent.

Suggestions have been made from time to time, generally in the patent literature, to employ specific hydrogenated oils for chocolate fats, or again, to convert the whole or part of the fat into diglycerides (by treatment, for example, with glycerine at an elevated temperature under reduced pressure), the diglycerides being supposed by some to yield a more homogeneous structure in the solid state and to have improved digestive properties. There is no reason to believe, however, that any of the proposals of these kinds which have hitherto been put forward have met with any extended application in technical practice up to the present.

CHAPTER V.—LARD AND LARD SUBSTITUTES

THE fats described in this chapter are exclusively used in cooking operations, including the production of bread, cakes and pastry, biscuits and fried materials.

Just as milk butter was the conventional staple fat employed for direct consumption, so lard and suet were formerly (with butter in certain cases) the fats which were exclusively relied upon for cooking processes of all kinds. These are now supplemented by various prepared fats generally known as lard substitutes or lard compounds, which are derived increasingly from vegetable sources.

The uses of fats in many forms of cooked food, *e.g.* cakes, biscuits, and pastry, are twofold : (i) merely to increase or form the fat-content of the product, for which purposes suet, butter, or margarine are frequently used in addition to lard, and (ii) to produce a “shortening” effect, *i.e.* a tendency in the product to be crisp and flaky, notably in pastry and biscuits, and it is found that this result is best attained when the incorporated fat is of a soft, granular texture, fairly firm but in no sense brittle or over-coherent. Lard possesses this combination of physical properties to a greater extent than any other natural fat, but in addition it is now closely simulated in the various blended mixtures which, as stated, go to form the group of lard substitutes.

The chief characteristics and varieties of natural lard and suet have been described in Section II., Chapter II. (pp. 136–137), and Section III., Chapter I. (p. 214).

Lard.—Enormous quantities of high-grade edible lard are produced annually, especially in the Middle West of the United States, most of it coming on the market in the form of neutral and leaf lards.

The usual specification for edible lard of these qualities is that of the United States Legislature : "the rendered fat from slaughtered healthy hogs, free from rancidity and containing no more than 1 per cent. of substances other than hog fat"; it will be observed that by this definition edible lard includes fat obtained from any part of the animals and not necessarily from the kidney and back fat.

Suet, etc.—For home cookery suet is of course often retailed with a certain amount of the tissue, *i.e.* it has not been rendered but is taken direct from the carcase and cleansed. Suet is also cold-rendered on the large scale in tallow factories and marketed as the pure fat free from tissue; whilst the best qualities of "premier jus" or edible tallow are also used largely in the manufacture of cooked cereal foods in bulk by bakers, pastry makers, etc.

With the exception of "premier jus" or oleostearines, suet substitutes as such are not met with, the substituted fats being confined to the two classes: margarines in place of cooking butter and lard compounds in place of lard.

Lard Substitutes or Lard Compounds.—The aim of the maker of these materials is that they may approximate as closely as possible to the physical consistency and texture of lard, when it is found that a similar "shortening" or crispening effect takes place during the baking of the mixture in which the fat has been incorporated.

The first lard compounds were made by intimate mixture of oleostearin or premier jus from tallow with a liquid vegetable oil such as cottonseed or maize oil, in the melted state, followed by rapid chilling. For the latter purpose it is usual to employ a cooling drum similar to that described on p. 303. For lard compounds a single drum, chilled by interior circulation of refrigerated calcium chloride solution to below -10° C. or even somewhat lower, rotates slowly, picking up the prepared mixture from a feeding-trough and carrying it round for about three-quarters of a revolution, when it is removed by a scraper and falls into another trough fitted with a longitudinal propelling screw similar to that used for margarine. The action of the screw not only

passes the chilled fat on to the packing department, but beats it up and converts it into a very fine, granular, opaque mass closely resembling lard in appearance.

Lard itself is, at the present day, as a matter of fact, usually cooled on a chilled drum of the same type after rendering and straining from tissue, in order to produce the most desirable and uniform consistency in the finished material.

More recently, lard compounds have been made extensively, especially in the United States, by the partial hydrogenation of suitable liquid fats, cottonseed oil being most widely employed, although other oils such as maize oil, sunflower oil, or whale oil are not unsuitable.

The oil, after preliminary refining by alkali, is hydrogenated to a melting point of about 30–35° C., the corresponding range of iodine value being about 80–60. The hydrogenated oil is further refined and deodorized in the usual manner for edible fats, and is then cooled and finally chilled as described above in the case of the simple lard compounds.

These products are in every way as suitable as the beef stearin-cottonseed oil type for lard substitutes, and on theoretical grounds it would appear that textures fairly closely approximating to that of lard itself might be expected, notably in the case of hydrogenated cottonseed oils. There is considerable similarity in the mixed glycerides present in the latter products, at iodine values of about 60–65, to those in lard.

Other "shortening" fats are now in frequent use in the production of pastries, cakes and biscuits. Different proprietary brands are available, consisting mainly of a hydrogenated fat which may be either hydrogenated cottonseed, groundnut or soya bean oil. At the present time hydrogenated groundnut oil is probably more used than either of the others in this country, but this is largely a function of the relative availability of the oils in question.

The employment of a straight hydrogenated fat of suitable iodine value in "shortenings" is often modified by

mixing a comparatively hard hydrogenated product, say, of m.p. 50–55°, with some of the refined and deodorized, but not hydrogenated oil ; or by mixing two qualities of hydrogenated fats, *e.g.* a harder product of m.p. 40–45° (iodine value 50–60) with a softer product of m.p. 20–25° (iodine value 80–90). The consistency of blended hydrogenated fats of this kind is sometimes found to be more suitable for cooking fats for pastry and biscuits than that of a straight hydrogenated fat. From another standpoint, mixtures of a hard hydrogenated fat and the original oil will be less prone to give trouble due to "hardening flavour," but will have more tendency to rancidity on account of the linoleic glycerides present in the unhydrogenated portion of the "shortening"; whereas oxidative rancidity will be less likely in the case of mixtures of relatively hard and relatively soft hydrogenated fats, although there may be somewhat more tendency to development of "hardening flavour."

Modern practice favours the use of fats melting at about 40° or slightly higher for baking crisp biscuits or pastry and, whether produced by blending harder and softer hydrogenated fats or otherwise, the risk of off flavours due either to rancidity or "hardening" should accordingly be reduced.

Fats for Frying.—It should be added that fats specially suitable for frying purposes now receive attention, the fried fish industry alone consuming sufficient quantities of fats to render the production of a particular grade of fat a commercial proposition.

Ordinarily, of course, and in kitchen practice, "dripping" or heat-rendered tallow fat is employed for this purpose, but for larger scale cooking operations special fats are supplied. These may be oleostearin-vegetable oil mixtures of somewhat stiffer consistency than the usual "lard compound" or, more usually, may consist of specific vegetable fats hydrogenated to a suitable degree (*e.g.* m.p. 35–40°). The presence of unhydrogenated vegetable oils of the cotton-seed or other "semi-drying" type in frying fats is undesirable, because the exposure to high temperature (with free access of air) during frying naturally causes oxidation and

polymerization of the linoleic glycerides present, resulting in rapid thickening of the oils during use.

There is perhaps not a great deal of difference between the preparation of frying fats and of the "shortening" fats previously discussed; it does not appear, however, to be absolutely necessary in the present case to chill the finished fat on a refrigerated drum, so long as the cooling is sufficiently rapid to prevent any undue separation into liquid and solid (fat crystal or stearin) phases.

CHAPTER VI.—THE NUTRITIONAL VALUES OF THE VARIOUS TYPES OF EDIBLE FATS

THE value of fatty products as foods has to be considered from several points of view :

- (i) The food value and digestibility of the various fats *per se* ;
- (ii) The influence of small amounts of non-fatty material introduced unintentionally during processing or intentionally as preservative, colouring matter, etc. ;
- (iii) The presence or absence in edible fats of the vitamins —A, —D, and —E.

Food Value and Digestibility of Fats per se.—In a general way it is true to state that any mixture of fats or single fat which melts completely at not higher than 40–45° C. is almost completely assimilated by the human organism without difficulty. At the same time the softer fats are more readily digested than the harder ones ; and again, a very hard fat which melts above, say, 50° C. is not assimilated to any extent when ingested alone, although if blended with a liquid fat so that the mixture is completely liquid by 40° C. it will be largely absorbed.

It seems reasonable to conclude that the essential factor is that the edible fat shall be completely liquid, or almost so at the temperature of the human digestive organs, and that, so long as the fat is present in the liquid state (in which alone, probably, it can be dealt with by the appropriate enzymes), it is immaterial whether it is an individual liquid glyceride or a liquid solution of a number of glycerides in one another, some of which may individually have melting points above the body-temperature. Needless to say, the latter case is that which obtains almost exclusively in all edible fats.

From a somewhat different aspect a distinction may be drawn in favour of the softer fats under certain conditions : the fats, like the carbohydrates, are mainly utilized in the production of bodily energy or heat, and do not contribute directly to the building up of tissue (although to some extent they are deposited in various parts of the body-tissues as reserve materials). As regards relative rapidity of assimilation and breakdown with release of heat-energy, it has been shown that the unsaturated fats are more readily disposed of than the saturated compounds, and for this additional reason the softer fats, containing more unsaturated derivatives, are more suited for edible purposes in the relatively cooler climates.

Comparing these generalizations with the chemical composition of butter and lard on the one hand and their substitutes on the other, it is seen that broadly speaking the latter, as manufactured at the present day, are, as regards their chemical composition and physical texture, in every way the equivalent of the former class. It is true that butter is characterized by the presence of a small amount of butyric acid combined as mixed glycerides, but it has yet to be demonstrated that these constituents have any definite physiological effect lacking in the cases of glycerides derived from fatty acids of higher molecular weight. In the case of lard, the resemblance between actual substance and substitute is closer in that the component fatty acids are practically of the same molecular complexity and closely similar structure in all cases.

Moreover, there is no evidence to show that glycerides of acids such as oleic, linoleic or linolenic, or of the various structurally isomeric forms of these acids, exhibit detectable differences in food value, and therefore it is to be concluded that the glycerides produced by partial hydrogenation of the more unsaturated oils are just as readily disposed of as the natural fats—a conclusion which is substantiated by the results of exhaustive feeding tests on human subjects which have been carried out on the Continent.

The position may be summed up by saying that, except

in very minor details, the chemical components of present-day margarines and lard compounds are the same as those of ordinary butter and lard, and this applies equally to the case of hydrogenated fats. From the chemical standpoint the substituted fats are an almost exact replica of the types present in the "natural" edible fats and are equally satisfactory.

As showing the range of variability which could be permitted, were it necessary, in the chemical structure of edible fats, it may be recalled (*cf.* Section II., Chapter IV., p. 184), that the glycerol of fats has been shown to be replaceable without detriment to nutrition by other alcohols such as mannitol or the hexoses, a structural change which is far greater than any introduced into the fatty acid side of the glyceride molecule in any of the present substitutes for butter or lard.

The Influence of Small Amounts of Non-fatty Materials introduced either Adventitiously or as Preservatives.—This is a somewhat wide subject which may be best treated concisely by a short review of the various kinds of impurities which might be encountered. It is probably unnecessary to mention here that the most dangerous adventitious materials in edible fats would be harmful bacteria introduced owing to lack of cleanliness in the apparatus employed, because in modern practice, whether the products are butter, lard or margarine or lard compounds, due care is exercised throughout the processes to avoid contamination by rigid attention to hygienic conditions.

In the various treatments applied to fats prior to their incorporation in the final products traces of the following impurities might be left in the products :

Free fatty acid owing to imperfect neutralization or *soap* left by inefficient washing : the free acidity should be reduced to below 0·2 per cent., larger proportions being betrayed by a slight characteristic taste, but not being definitely harmful to the human organism, whilst traces of soap, similarly, are not harmful but are readily detectable by unpleasant flavour.

Hydrogenated fats may contain exceedingly small proportions of *metallic nickel* (of the order of 1 part per million), but it has been proved that as much as 0·5 gram of nickel can be ingested per day without toxic effect, and the minute amounts possibly present as a result of the presence of a proportion of hydrogenated fat cannot conceivably exert the slightest harmful effects.

The *unsaponifiable matter* accompanying the fats employed, although only in small proportions, has an important influence on the character of the product. A few tropical fats, as previously mentioned, are liable to contain poisonous constituents in the unsaponifiable portion, and such fats are of course unable to be used for edible purposes. A much more general feature of the unsaponifiable matter, which consists largely of sterols, is the exceedingly beneficial part played in nutrition by the vitamins, a subject which is further dealt with below.

Few, if any, other impurities than those mentioned are likely to be left in the fats or to be introduced during processing, it being taken for granted here that the chemical agents employed—alkali, mineral acid, adsorbent earths or charcoal, etc.—are of a quality free from toxic compounds such as traces of arsenic, lead, etc.

It is quite possible, on the other hand, that more harmful constituents have been added to edible fats as “preservatives” than are likely ever to be introduced by accident during their refining and preparation. This subject has already been mentioned when dealing with margarine, and it was then pointed out that preservatives directed against the development of rancidity by bacterial agency are in general liable adversely to affect the human organism and, moreover, the effect of such compounds is often cumulative, owing to their retention in the digestive system. Undoubtedly the only safe preservative, and one of the most efficient, is sodium chloride, and beyond this the safest plan is to ensure that edible fats are consumed within a reasonable time of their manufacture (*i.e.* a few weeks), in the course of which, if prepared and stored in closed packages

under modern conditions, they should readily remain in a state of freshness.

The Presence or Absence in Edible Fats of the Vitamins —A, —D, and —E.—The important subject of vitamins has received much general attention within the past few years, but it is possible here to refer only to the fat-soluble classes. It has been proved that there are materials present in natural foods which are not enzymic in character and are present in extremely minute amounts, but which nevertheless are essential to the growth and maintenance or renewal of the animal organism. The fat-soluble vitamins A, D, and E are those which are essential to healthy growth, especially of the young, and their presence in fats offered as substitutes for butter (in which they are present to a sufficient extent) becomes a matter of considerable importance.

Whilst some natural fats, such as beef tallow and a number of raw vegetable oils, contain a certain proportion of one or all of the three vitamins, others are almost completely devoid of them, and in no case does the vitamin potency of any oil used in the edible fat industries approach that of good dairy butter. Furthermore, the vitamins are destroyed, or liable to be destroyed, by excessive heat, at all events in presence of traces of oxygen. Consequently fats which have been hydrogenated at a high temperature, or which have merely been subjected to refining and deodorization by processes involving temperatures above, say, 150° C., are usually almost completely deficient in vitamins or, at all events, active growth-promoting properties.

It is therefore clear that, in this respect only, refined and deodorized fats may be inferior in food value to ordinary butter, and the problem of increasing or renewing the vitamin-content of these substituted fats has received much attention from detached research workers and also from the industries concerned.

So far as vitamin D is concerned, this can be produced by irradiation of most refined fats with ultra-violet light. The sterols present in these fats usually include small pro-

portions of ergosterol which passes into vitamin D (or one form thereof) when thus irradiated. The problem of vitamin-A introduction cannot be solved in the same way and therefore the practical solution found has been to obtain concentrates of both vitamins from suitable sources and to add the necessary proportion of these to the prepared margarine fat.

As already mentioned (p. 304) certain liver oils relatively rich in the vitamins provide the technical source of the latter. Cod liver oil, for example, contains about 50 times, and halibut, whale or ox liver oils perhaps 2,000 times as much vitamin A as summer butter, the proportions of vitamin D being more or less in similar ratios. It is thus clear that the unsaponifiable fraction (amounting to very few per cent. of the oil) of a fat such as whale liver oil will represent an exceedingly rich concentrate of the vitamins. Addition of a minute proportion of such concentrates to the prepared margarine fats confers the desired vitamin potency.

Separation of the unsaponifiable matter from a fat such as whale or ox liver oil by processes which avoid as far as possible destruction of the vitamins present, followed by addition of determined proportions of the extract to the prepared fats so as to give a vitamin content equal to that of summer dairy butter, is therefore the procedure followed in the production of "vitaminized margarines."

It should be noted that the use of the unsaponifiable concentrates has a further advantage, namely, the avoidance of introducing, with the vitamins, the highly unsaturated glycerides which are always present in the liver oils concerned, and which would increase the tendency of the margarine towards oxidative rancidity (p. 329).

CHAPTER VII.—THE PROBLEM OF RANCIDITY IN EDIBLE FATS

THE preservation of edible fats in a fresh state is a matter of urgent importance and also of some difficulty, because fatty matter is an excellent medium for the growth of many forms of moulds and bacterial life and also, when unsaturated glycerides are present, is very prone to incipient oxidation at the ethylenic linkage.

A definitely rancid fat proclaims itself, of course, by odour and taste, but it is not so simple to determine the presence of rancidity in the earliest stages of development.

The subject is one which is receiving constant attention, and somewhat contradictory and dogmatic statements have appeared in the literature with reference to the underlying causes. A brief account will therefore be given of the various factors which are at present known to favour rancidity, with some indication of their possible mutual effects.

The following tests for incipient rancidity illustrate in a few words the characteristic products which may be developed :

Oxidation Products.—Several workers have elaborated tests which indicate the comparative extent to which a fat has been converted into volatile products of an aldehydic or ketonic nature, and those introduced by Issoglio and by Kreis will serve to indicate the underlying motives.

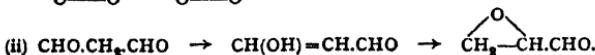
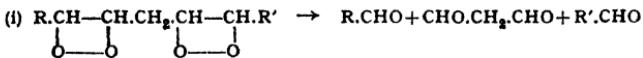
Issoglio recommends a procedure which is reminiscent of the Reichert-Meissl method for indicating the proportion of volatile fatty acids in a fat, but in Issoglio's test it is the volatile aldehydes or ketones produced by oxidation as the fat becomes rancid which are the object of attention : a definite weight of fat is thoroughly shaken with distilled

water for two hours and is then filtered through a moistened filter-paper and an aliquot portion of the aqueous filtrate is acidified, boiled with a definite volume of N/100 permanganate for five minutes, cooled, mixed with the same volume of N/100 oxalic acid (containing sulphuric acid) and titrated back with N/100 permanganate. From the amount of permanganate consumed in oxidizing the volatile aldehydes a figure which Issoglio terms the "oxidizability value" is arrived at, which is taken as a measure of the rancidity, *i.e.* rancidity is implicitly assumed to lead in all cases to the production of volatile bodies of a carbonylic type.

The Kreis test for rancidity, which as improved by Kerr is very largely made use of at the present day, consists in shaking a dilute ethereal solution of phloroglucinol with the fat in presence of hydrochloric acid, when a delicate pink coloration appears in case of rancidity. By carrying out the test under standardized conditions the intensity of the pink colour can be made in some degree a quantitative measure of the rancidity of the fat ; the validity and efficiency of the Kreis test (which, as a colorimetric method, requires careful scrutiny) have been and continue to be the subject of numerous investigations. The mechanism of the Kreis test was shown by Powick to be due to the presence in rancid



fats of epihydriol aldehyde (or its acetal), $\text{CH}_2-\text{O}-\text{CH}(\text{OH})-\text{CH}_2\text{CHO}$, which under the conditions of the reaction yields a red condensation product with phloroglucinol. The mode of formation of the epihydriol aldehyde has not been cleared up, but it could conceivably result from the further decomposition of a peroxide of a linoleic or other polyethenoid glyceride somewhat as follows :



Täufel and co-workers have considered exhaustively the Kreis test in terms of measurement of epihydriol aldehyde, and have suggested further standardization of the method

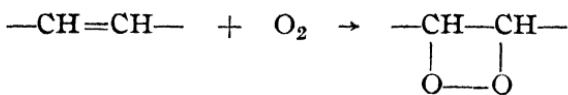
by which it is claimed that one part of the aldehyde can be detected in ten million parts of fat.

Other procedures for evaluating rancidity are the Schiff, Schibsted and Lea tests, which depend on other reactions for the detection of aldehydic products of decomposition of unsaturated acyl chains. The Schiff test for aldehydes (restoration of colour to a fuchsin solution decolorized with bisulphite solution) was standardized as a measure of fat rancidity by von Fellenberg. Schibsted shook a solution of the fat in petroleum ether with a standard solution in 50 per cent. alcohol of rosaniline hydrochloride decolorized with sulphur dioxide, and matched the coloration redeveloped in the petroleum ether layer against a standard solution of cresol red kept at $pH\ 8.3$. Lea has advocated a direct measurement of the amount of bisulphite fixed by aldehydes present in 1 gram of rancid fat. The fat, in benzene solution, is shaken mechanically with a solution of sodium bisulphite for an hour at 20° in the dark. The resulting emulsion is centrifuged and an aliquot portion of the aqueous layer titrated with iodine until the excess of bisulphite is just destroyed. Sodium bicarbonate is then added to liberate the aldehyde from its bisulphite compound, and the liberated SO_2 also determined by titration with 0.002N iodine solution. The aldehyde content is expressed as c.c. of 0.002N iodine per gram of fat; fresh fats show values not exceeding 0.1–0.2 c.c., whereas moderately rancid fats may give values up to 10 c.c.

All the foregoing tests are directed to assessing oxidative rancidity from the presence of some of its characteristic products—aldehydes of fairly low molecular weight. It is important, on the other hand, to know at the outset the likelihood of a given sample of fat to develop oxidative rancidity, rather than to have a relative indication of the extent of this deterioration when the latter has actually set in. From this point of view the measurement of organic peroxides which are among the early products of atmospheric oxidation of unsaturated fats has proved of some value.

It is well known (*cf.* p. 330) that the first definite chemical

alteration which takes place when an unsaturated fat is attacked by gaseous oxygen is the formation of peroxidic compounds at the ethylenic linkages :



These peroxides liberate iodine from hydriodic acid and standard methods have been devised for making the determination quantitative. The fat (1 gm.) is treated under prescribed conditions with a solution of potassium iodide in acetic acid mixed with chloroform or carbon tetrachloride. At the conclusion of the operation the liberated iodine is titrated with 0.002N thiosulphate and the "peroxide value" expressed in terms of c.c. of 0.002N thiosulphate per gram of fat.

A simple method described by Lea is as follows : 1 gram of the oil or fat is weighed into a Pyrex test-tube, approximately 1 gram of powdered potassium iodide and 20 c.c. of glacial acetic acid and carbon tetrachloride (or chloroform) mixture (2 : 1 by volume) added, and the liquid heated to boiling over a small flame impinging on the bottom of the tube. Boiling may be continued for half a minute, the heavy vapour of the solvent minimizing the diffusion of oxygen back into the tube. The tube is then cooled under the tap, the contents poured into 30 c.c. of water and titrated with 0.002N thiosulphate. Low peroxide values should be controlled by a blank on the reagents. For highly rancid or oxidized fats the amount of fat used should be reduced, e.g., to 0.5 or even 0.1 gram.

Other forms of the same test have been proposed by Taffel and Revis, and by Wheeler.

It has been observed by various workers that susceptibility of fats to atmospheric oxidation is much accelerated by light, notably by ultra-violet rays of wave-length 290–400m μ and also by visible rays in the blue region of the spectrum of wave-length shorter than about 500m μ , whilst light of longer wave-length is comparatively or wholly inert. This has led to proposals to employ for fats coloured

wrappers which will not transmit light of the active wavelengths, as an assistance in retarding the onset of oxidative rancidity. It has also been made the basis, by Lea and others, of "accelerated oxidation tests," in which films of edible or other fats are exposed to light of definite intensity under standard conditions whilst also exposed to air, and their peroxide values determined after successive periods. From the increase in peroxide value the relative stability of a fat to oxygen can be fairly accurately assessed. It is possible, for instance, to estimate the number of weeks during which a given sample of fat will keep free from rancidity with exposure to air and diffused light by means of "accelerated" tests by irradiation which occupy relatively few hours or, at most, days.

It must be borne in mind that the organic peroxides formed during atmospheric oxidation of fats are a transitory phase, and pass in time into other products which contain no reactive oxygen. Thus it may happen that a very rancid fat may possess quite a low peroxide value. This circumstance has sometimes cast doubt on the worth of the peroxide value in assessing oxidative rancidity. It must always be remembered, however, that this test depends largely on the previous history of the fat, and that it is fully informative only when applied to relatively fresh fats, and best when in the form of a series of "accelerated oxidation" tests. In these circumstances it has the merit, as compared with other methods, of detecting liability to development of rancidity instead of merely indicating the degree of rancidity already reached.

Odoriferous Compounds.—In pronounced cases of rancidity oxidation proceeds so far that short-chain acids such as butyric, valeric, or caproic make their appearance and of course the fat acquires a correspondingly pronounced odour. Other cases are well known, however, in which little or no intensive disruptive oxidation has occurred, where a heavy odour reminiscent of certain aliphatic esters, but probably due in reality to methyl nonyl ketone and allied compounds, betrays the presence of rancidity. This form

of rancidity is definitely to be ascribed to enzymic action on the fats, the enzymes being developed by moulds or fungi which have become established in the fat; it is favoured by anaerobic conditions, *i.e.* by the exclusion of oxygen from the fat, and is in no way to be ascribed to the action of atmospheric oxygen.

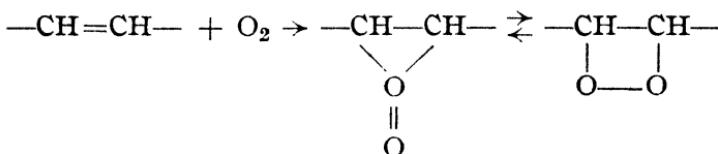
Development of Free Fatty Acid.—Frequently rancidity is accompanied by considerable increase in the free acidity of the fat, but the purely oxidative type of rancidity and hydrolytic rancidity do not by any means always take place at the same time—a fat may be highly rancid whilst its acid value may not have increased to more than a comparatively slight extent. Consequently, whilst development of free fatty acid is a sure sign of marked rancidity, the absence of any sensible increase in free fatty acid is no criterion of freedom from rancidity.

Causes of Rancidity.—Whilst, as frequently happens, the study of rancidity is complicated by the simultaneous action of several factors which may contribute to the final result, the main causes of rancidity may be assigned to two divisions, atmospheric oxidation and enzyme action (whether of hydrolysis, oxidation, or other nature):

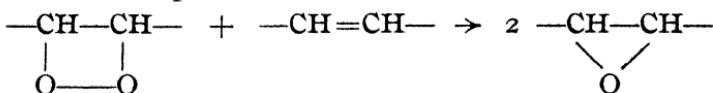
(i) **Atmospheric Oxidation.**—The chemical changes concerned in the onset of oxidation of an unsaturated fat by atmospheric oxygen at the ordinary temperature are essentially the same as in the early stages of oxidation of "drying" oils, for example, a film of linseed oil exposed to air, or linseed oil or other fatty materials "blown" with air or oxygen at a relatively high temperature. The phenomena of incipient rancidity should therefore be considered in conjunction with the wider case of more extensive oxidation of unsaturated fats, which is the subject of discussion in Section VIII, Chapter I. (pp. 461-466).

In oxidative rancidity, as in the more drastic type of attack by gaseous oxygen, oxidation is confined to the unsaturated linkages of the fatty acid chains, and neither the glyceryl radical of a fat nor the free carboxylic acid group in a fatty acid are directly concerned in the oxidation.

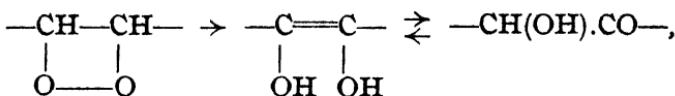
A pure unsaturated fat—e.g. an oleo-glyceride or, even more readily, a linoleo-glyceride—will commence to absorb oxygen on exposure to air at the ordinary temperature. In the initial phase the process is almost one of physical solution rather than chemical combination, for the added oxygen can be at least partly removed simply by heating to 100° at a reduced pressure. But the growing capacity of the fat to liberate iodine from hydriodic acid solutions, and similar properties, indicates that concurrently an organic peroxide is produced, perhaps according to the scheme :



Formerly it was supposed that the peroxide might interact with a further unsaturated radical, giving two molecules of an oxido-compound :



This conception does not agree, however, with the known facts that approximately two atoms of oxygen are taken up by each ethenoid group, and that oxido-acids, or the poly-hydroxystearic acids into which the latter pass, are definitely by-products of the atmospheric oxidation process and are found only in subsidiary proportions. Ellis developed a view originally mentioned by Fahrion, namely, that the peroxides undergo rearrangement into isomeric forms :



and Morrell, in the cases of air-oxidized methyl β -elæostearate and similar compounds, has given definite proof of the existence in the oxidized materials of the α -hydroxyketonic derivatives. So far as oxidative rancidity is concerned, it is the subsequent by-products of decomposition of the peroxides or their isomerized forms which are mainly

responsible. As indicated on p. 325, simple rupture of the carbon chain at this point may afford either fatty aldehydes of low molecular weight or epihydrin aldehyde, whilst it is conceivable that the peroxides themselves may possess a definite flavour. Very possibly such further changes are accelerated by light and by other conditions such as the degree of acidity (ρH) of the system, whilst moisture may exert a retarding or an accelerating effect.

From the standpoint of rancidity, it is important to consider not only the mechanism of the oxidation process but also how the latter is accelerated or retarded by the presence of minute concentrations of various substances.

Atmospheric oxidation of fats can be stimulated by various compounds. The process is autocatalytic, *i.e.* the organic peroxides themselves act as positive catalysts and, once present in small proportions, accelerate the fixation of oxygen by the remainder of the unsaturated fat. Other substances also accelerate the process.

Many metals, and their salts, for example, are especially vigorous catalysts of oxidation in this respect. Cobalt, copper, vanadium, iron, manganese, nickel and chromium, and their compounds, are most active in this respect, whilst tin and aluminium have little action. It is thus desirable to avoid the presence of traces of these metals (in practice, especially copper and iron) in edible fats. Vessels used in their production should, if containing iron, be constructed of one of the resistant alloys such as a nickel-chromium steel or, where possible, of aluminium. If more than one metal is used in plant fittings, the possibility of contact-corrosion at the metal interfaces should be carefully watched.

It should also be mentioned that certain complex natural organic compounds, such as pigments of the type of haematin or enzymes of the peroxidase group, can act as positive catalysts in the addition of oxygen to unsaturated fats. Care should accordingly be taken to remove, or exclude, any traces of these substances from fats destined for edible purposes.

Another important group of compounds act in the reverse direction—as retarders or inhibitors of atmospheric oxidation of fats. Members of this group are certainly present in the seed endosperms from which most vegetable fats are taken, and therefore appear in traces in the raw fats. Such fats exhibit a lag or "induction period" of varying duration before oxidation sets in, and this period is now generally attributed to the time necessary for the destruction by oxidation of the compound or compounds which are preventing the oxidation of the fat. The theoretical aspects of the retardation of oxidation of a large number of molecules of unsaturated compound by relatively few molecules of an "inhibitor" or "anti-oxygen" have been discussed by Moureu and Dufraisse and by Christiansen.

The natural inhibitors (termed "inhibitols" by Olcott and Mattill) which may occur in raw fats are probably of several distinct kinds. Olcott and Mattill have shown that vitamin E (tocopherol) and related compounds have considerable efficiency in retarding oxidation of fats; Hilditch and co-workers observed that seed cakes from which the fat had been removed were richer in antioxygenic material than the extracted fats, and found evidence that their antioxygenic concentrates resembled carbohydrates in reducing properties and that one at least of the active principles present was of an amphoteric nature and contained either basic nitrogen or, perhaps, basic oxygen. It seems very possible, however, that the essential grouping in all these natural antioxygenic compounds is a polyhydroxyphenyl residue, present in a complex molecule which may vary in kind, e.g. tocopherol, gossypol, or even a derivative of the anthocyanins or flavones.

This latter statement is supported not only by the known presence of polyhydroxyphenyl nuclei in the naturally occurring compounds mentioned, but by the fact that hydroquinone and pyrogallol, with other simple polyhydroxyphenols in lesser degree, show very strong antioxygenic properties when added in minute proportions to fats. Other substances with similar properties include many

substituted amino-compounds (*e.g.*, diphenyl-*p*-phenylene-diamine, diphenylhydrazine, amino-phenols), many thio-amino-compounds, cyanamide compounds, sulphites, phosphates, etc.

The practical question of suppressing or retarding rancidity by the addition of suitable antioxigenic compounds cannot, however, be said to have been satisfactorily solved. Most of the compounds mentioned in the previous paragraph, so far as edible products are concerned, are ruled out by reason of toxicity. The naturally occurring antioxigenic compounds have not yet been isolated in the form of concentrates sufficiently pure (and, especially, pale-coloured) to be used practically in edible fats, but Musher has advocated the use of cereal or soya bean flour as an inhibitor of oxidation in certain fats, whilst the use of salts of phosphoric acid has also been proposed.

(ii) **Enzyme Action.**—It is to this class that the complications of the rancidity problem are mainly due. Mould-spores may infect the fat and the resulting moulds contain a variety of enzymes, each of which may find some work to do according to its particular bent. *Lipoclastic enzymes*, if the medium is suitable to their development, will tend to the production of free fatty acid. There is some evidence that *enzymes of the peroxidase type* also induce oxidation effects, not only of the same nature as atmospheric oxidation, but also in the case of saturated fatty acids, which may be converted by oxidation at the β -carbon atom from the carboxyl group into ketonic acids and ultimately into methyl ketones :



Oxidation of saturated acids in this way occurs infrequently in comparison with that of the readily oxidized unsaturated fatty acids and is of an entirely different type ; but it is for this reason that the statement, sometimes met with, that unsaturated fats alone undergo oxidation during rancidity changes must be looked upon as incorrect.

Lastly, as mentioned on p. 329, it is known that specific

moulds flourish on certain types of fat in absence of light and air, and that the chemical products of their metabolic changes include bodies of a methyl ketonic nature; in such cases it is probable that moisture accelerates the progress of rancidity.

Whilst, therefore, the complicated question of the causes contributing to rancidity of edible fats has not yet been thoroughly unravelled, sufficient is known to emphasize the fact that fats prepared for edible purposes, and required to be stored for any time prior to use should be kept perfectly sterile and not exposed to contamination by harmful organisms and should also, as far as possible, be excluded from contact with the atmosphere.

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SECTION V.—THE SOAP INDUSTRY

Introductory.—The soap industry is even more complex than the edible fat industry in the ultimate forms in which its products come on the market, and an attempt will be made in the succeeding chapters to collect together first of all, as far as possible, the description of the procedure which is common to nearly all forms of soapmaking, thereafter proceeding to deal with the more important classes of soaps and other detergents at present in general use.

The chapter which follows, therefore, gives some account of the methods of soapmaking, both in the pan or by cold process, and takes the soap up to the point at which it is ready to be transformed, by submission to a further sequence of processes mainly non-chemical in nature, into either toilet or household bar soaps of various qualities, soap flakes or powders, or textile (industrial) soaps.

Before proceeding to a description of the latter products in more detail, a chapter is interpolated on the physico-chemical nature of soap, both in the "genuine" state and in solution, and on the changes in state which take place from the point at which it is first formed by saponification of fat by alkali until it reaches its final form. The extent of our knowledge of these matters, from a scientific standpoint, has advanced considerably in the past twenty years, although the picture is still far from complete.

The remaining chapters of the section deal with :
the preparation of soaps for toilet use ;
the production of the several varieties of bar soaps for general household use ;
the manufacture of dry soaps as flakes or in powder form ;

the production of soft soap and the chief types of soap used in the important textile industries ;

the discovery and development of a variety of detergent materials with special properties, which are, chemically speaking, not soaps, and which may be grouped together for convenience as "Soapless detergents."

It is not very easy to give a proportionate impression of the relative amounts manufactured annually of any of these materials, nor of the extent to which the use of the different qualities varies.

There is far less deliberate adulteration of soap practised now than formerly, *i.e.* deliberate "filling" of a soap with cheap inert materials in order to employ as little as possible of the more costly fatty material, whilst selling at as high a price as possible. All the soap made by the large manufacturers, whatever the fat-content, is sold at prices which are more or less in proportion to the cost of the ingredients ; thus, for example, although very large quantities of "run" soaps containing about 45-55 per cent. of fatty materials are sold in addition to the "genuine" soaps with 63 per cent. of fatty materials or their rosined varieties, the former are good soaps appreciated by the public, the deficiency in fatty acid is made up by the detergent action of the silicate or carbonate present, and they come on the market at a cheaper price than the "genuine" soaps.

Similarly, the dry soaps and powders, of a variety of kinds which are produced in ever-increasing quantities for specific uses, meet a large demand and are sold at reasonable rates ; a dry "genuine" soap flake, of course, contains a considerably higher percentage of fatty matter than the same soap in bar form, and is also more readily brought into solution.

The new types of "soapless detergents," including the salts of monosulphuric esters of higher fatty alcohols, oleyl derivatives of β -amino- or of β -hydroxy-ethylsulphonic acid (the Igepons), and many other compounds, nearly all characterized by the presence of an acyl group containing a long normal chain of carbon atoms, are finding increasing use, especially as "textile assistants" in scouring, bleaching,

dyeing, finishing and stripping cloth fabrics. Some of them, weight for weight, have far greater dexterity than ordinary soaps. Some possess special properties such as capacity for wetting surfaces ("wetting-out agents") whilst others have pronounced emulsifying powers or, again, are efficient agents for dispersing insoluble finely-divided or colloidal solids through an aqueous solution. Most of these new, semi-synthetic products, moreover, are as active in hard water or sometimes even in presence of dilute mineral acids as when in solution in pure water.

CHAPTER I.—MANUFACTURE OF GENUINE SOAP IN THE PAN, COOLERS AND DRIERS

Soap-boiling in the Pan.—The term “genuine soap” refers to the products of saponification of a mixture of fats (with or without rosin) as obtained after cleansing in the soap pan and before or without the addition of any non-fatty material such as silicate or carbonate liquor, fillers, etc.

The actual fats or fatty acids introduced into the pan are chosen qualitatively and quantitatively in order to yield a soap of particular qualities or complying with a given specification, and then converted into finished soap in the pan. The fatty material may be introduced either in the form of fat or of fatty acids prepared by the methods given in Section III., Chapter IV., pp. 270–278, or a mixture of both.

In either case the soap pan is of the type described in Section III., Chapter IV., p. 267, and the fatty material is converted into soap in the form of curd, as described on p. 269 in dealing with the saponification of fats, glycerine lyes, if present, being pumped away and settled for glycerine recovery.

The crude curd soap obtained after saponification of the fat or fatty acids requires re-washing before it becomes a genuine soap of good quality, free from alkali, salt, and other impurities.

This is effected by re-boiling the curd with just sufficient water to form a thick homogeneous liquid and subsequently continuing the boiling, whilst just sufficient brine solution is added to induce the re-formation of curd, which is again allowed to settle. This preliminary washing not only

removes alkali and salt from the soap, but also some glycerine which remains in the saline solution mechanically retained in the original curd, and the brine lye from it is therefore also worked up for glycerine.

The washed curd is again "closed" by boiling with a little water to the homogeneous liquid phase, and, if sufficiently clear (as is usually the case at this stage if the raw fats used were of good quality), it is next converted into "finished" soap.

In the case of rosined soaps (Chapter IV., p. 379), the addition of rosin may be carried out at this point and a third "graining out" with brine given.

The final stage (the "strengthening change") is to "close" the soap with water and boil gently with a little caustic soda for about five hours, finally "graining out" very cautiously with the minimum of caustic soda or brine by an experienced soap-boiler; the addition of electrolyte is carried on slowly, with continuous gentle boiling, until a very loose curd commences to form and breaks up on pouring into large, somewhat sticky fragments.

"**Fitting**" or "**Finishing**."—Boiling is still continued when this stage is reached, usually with no further addition of electrolyte, until the soap becomes closer, *i.e.* on scooping up a portion it falls away in small flakes not less than an inch or two in size, which slip away cleanly and leave no residual soap or greasy matter on the scoop employed. The art of "finishing" or "fitting" soap consists chiefly in stopping the final boiling at exactly this point, after the soap has commenced to "close" and before the flakes begin to cohere unduly. In the correct state the soap will coalesce on standing and form a homogeneous liquid mass from which the remaining impurities slowly settle. The free alkali content of the "finished" or "fitted" soap should not exceed 0·2 per cent.

The "fitted" soap is therefore left for some days at a temperature of about 60–70° C. whilst it "finishes," *i.e.* the remaining saline and alkaline aqueous solution slowly gravitates, with the impurities, to the bottom of the pan.

After about two to five days the settling or finishing process is complete and the contents of the pan consist of a thick layer of liquid soap (usually solidified in a thin crust at the top) resting on a small amount of "nigre" or "foots." The latter is a small layer of a weak solution of soap containing about 20-30 per cent. of soap and the bulk of the organic impurities, iron soaps, etc., which have settled from the finished soap. This narrow dark-coloured layer is characteristic of a "finished" pan; it is generally withdrawn separately and worked up again with similar material from other pans and cruder fats in the manufacture of lower-grade soap.

The whole operation of a soap charge takes about a week: saponification and graining out with brine twice is completed in two or three days (it should be possible to give at least two washes in the course of one day), whilst the final settling should be given a minimum of two, and better, four or five days.

The specific procedure adopted is governed entirely by circumstances, and maximum efficiency in the boiling and graining-out processes subsequent to saponification is secured by so working that the smallest number of these operations is necessary. To this end the contents of the pan must be so manipulated that each time the curd is produced in a loose form, which permits as ready gravitation as may be of the saline lye from between the soap granules or clots.

The removal of the finished soap is known in the trade as "cleansing" the soap pan, and is conducted by dropping a skimmer-pipe beneath the upper crust of solidified soap and running the liquid soap from the pan either through a pump, or, where possible, by gravity through large wooden ducts, into either the soap-frames or coolers, or very frequently into a crutching-pot prior to framing.

The nigre and final lye are subsequently disposed of as already indicated, and the pan is then ready for a fresh charge of fat and alkali.

The finished soap, which at this stage is in a liquid state,

contains about 64 per cent. of fatty materials as fatty acids. As marketed, it is of course a solid in the form of bars or tablets, and may contain this amount of fatty acids, or more, or less, according to the type and brand of soap.

The various processes employed for specific types of soap are dealt with in succeeding chapters of this section, but it may be noted here that a slightly lower grade of soap than the "genuine" soap obtained as described above in the pan results if the "finished" soap is grained out with somewhat more brine, so that a fairly open-grained curd is boiled on the lye and, when settled, just remains as a curd and not a homogeneous liquid soap. The entangled electrolyte cannot separate quite so completely from the discontinuous curd phase as from the homogeneous "genuine" soap, and consequently the final product contains somewhat more water and salt and correspondingly less fatty matter. These "curd soaps" are probably not on the market in such large quantities as formerly, and contain as a rule about 61-62 per cent. of fatty materials as fatty acids.

Crutching Operations.—Practically all soaps contain, in addition to the true soap, added matter of one kind or another. "Genuine" and "curd" soaps, made in the pan, are subsequently usually perfumed, coloured, or incorporated with an antiseptic such as cresylic acid, whilst in other classes of soaps additions may be made of detergents such as sodium silicate or carbonate or of inert "fillers" such as talc, china clay, chalk, starch, or other substances.

These additions are almost invariably made to the liquid soap as it comes from the pan and before setting aside to harden in frames or mechanical coolers, and the same type of apparatus, a "crutching-pot," is used in each case.

The crutching plant consists simply of a cylindrical steel or wooden vessel capable of dealing with a charge of from 15 to 30 cwt. of soap, and containing a vertical shaft with stout horizontal curved paddle-blades and fixed baffle-plates on the sides of the vessel. A jacket round the pan serves to maintain the soap in a liquid condition, low-pressure steam being used for heating, since it is not usually

desired at this point to effect any drying of the soap. The soap is usually run in from the pan at about 75° C. and crutched to a final temperature of about 55° C.

The requisite charge of finished soap is run or pumped into the crutching vessel from the pan and the correct amounts of perfume, dye, silicate or other liquor, or filler are added whilst stirring is in action. Agitation is continued for some little time until complete incorporation of the added compounds is effected, and the still liquid soap is then passed on to the cooling process.

So far as the "genuine" soaps are concerned, the additions in the crutching plant will simply consist of a small amount of perfume and/or dye, together with cresylic acid or carbolic acid in the case of carbolic soaps.

Soap Cooling.—The liquid soap after crutching is run by gravity or pumped into cooling-frames. These consist of iron frames designed for carriage on a low trolley, and are about 4 feet 6 inches long and high and about 18 inches in width. The sides are removable, the frame being clamped together externally by iron bolts.

The soap is left in the frames for a week, and during this period it slowly cools and solidifies to a homogeneous stiff solid; as soon as a skin has formed on top (after 10–12 hours) it is knocked down and compacted by mallet blows, and after a further 2–3 hours it is again stamped down with a heavier implement, after which it is left untouched until ready to be removed from the frames. The sides of the frames are then taken away and the solid rectangular block is cut up into a series of large slabs about 2½ inches in thickness by means of wires. These are transferred to barring or tabletting machines in which by a similar wire-cutting process the slabs are divided into long bars of about 2½ by 2 inches cross-section, which are piled transversely in loose stacks and left for a day or so to harden externally.

By a similar process the long bars of soap are re-cut into smaller bars or tablets of specified size. This machinery was formerly hand-operated, but is now largely mechanically operated, the long bars of soap travelling by belt conveyor

and being successively cut into tablets and then stamped, wrapped, and packed in cartons, all by the same machine.

The operations after the soap leaves the cooling frame are purely mechanical and directed towards the final appearance of the soap in an attractive form for sale and, together with the final wrapping and packing of the tablets, form phases of soap manufacture which, although highly important from the point of view of labour-saving appliances, sale value of the product, and mechanical engineering devices, do not involve any further chemical processes. It should, however, be noted that, so far as "genuine household soaps" are concerned, the manufacture is complete, except for cutting, tabletting, and packing, when the soap leaves the coolers.

Many devices have been patented for accelerating the cooling or setting of the soap so as to avoid the period of several days consumed in standing in the frames, thereby accelerating production and effecting considerable economy in the floor space required for the production of a given output of soap. One of the more widely used appliances is the Jacobi cooler, which is closely similar in construction to a filter-press. By an arrangement of channels between the plates of the cooler the cold inlet water, admitted at the bottom of one of the ends of the machine, is pumped up and drawn over each plate and finally emerges at the base of the last plate. The plates are so flanged that when the press is tightened up a rectangular space, equivalent in size to a large slab of soap, is left between each pair of compartments in which the water circulates, and liquid soap is run into these spaces and chilled rapidly by the cold water in the adjacent compartments. By this means the soap is cooled in the course of an hour or so to a condition in which it may be cut, stamped, and packed. The use of the Jacobi or other coolers has not been an unqualified success, complaints being frequently made that the quality of the soap made in this way is not equal to that from the frames.

These criticisms may well be sound in view of the following factors :

(i) The rapid cooling process involves the formation of a crust of solid soap enclosing the still liquid inner core, and owing to the low heat conductivity of the soap and to the rigidity of the outer crust the subsequent cooling is not only retarded, but there is an absence of flexibility in the cooling conditions which leads to the setting up of strain and sometimes to the formation of hollow spaces or cracks in the interior of the cooled slabs.

(ii) The physical changes undergone during solidification of soap are complex in nature and do not consist of simple change from the liquid to one solid phase. The solidified soap as first produced undergoes further changes in type, and, whilst originally probably a solid colloidal solution, is slowly transformed on standing at ordinary temperature into various phases, including the separation of actual crystalline soaps together with the formation of other colloidal soap phases. These changes, which lead ultimately to the production of a block of soap firm in texture throughout its cross-section, proceed but slowly and cannot be hastened. It is doubtless owing to the necessarily long time factor involved, amounting to several days, that attempts to hasten the cooling process have not been, and are not likely to be, completely successful.

The physical chemistry of soap receives some additional attention in the next chapter.

Soap Drying.—Whilst *genuine household soaps* are sold, so far as the state of the soap itself is concerned, practically in the condition in which they leave the pan (*i.e.* containing about 63-64 per cent. of their weight as fatty acids), a number of other important varieties of soap, including most *toilet soaps*, contain a considerably higher proportion of fatty materials. It has been explained above that the liquid soap prepared in the pan is characterized by a fixed content of about 63-64 per cent. of fatty material, and this can only be increased by removal of some of the water present by evaporation.

This forms the first stage of production of *toilet soap stock* on leaving the pan, and is effected, according to circum-

stances, by mechanical passage through a continuous drier, or in other cases by heating the soap, before or after framing.

In the latter method the soap is sometimes heated up in the liquid state, by means of a dry steam coil in a closed pan, until the requisite amount of moisture has been driven off ; or, more often, the bars of soap after " running " (*i.e.* mixing with diluents such as silicate or carbonate of soda, etc., in the crutching-pots) or other treatment are " stoved " by being placed on shallow trays in stacks in a long rectangular tunnel. This may be constructed with closely fitting sides made of asbestos composition in detachable portions, and is provided with a blower or fan at one end whereby air is circulated over the soap. The intake of air to the stoves is preferably heated, before it reaches the soap, by passage over a nest of steam-heated pipes, whilst, alternatively or in addition, the whole of the stove may be heated to a suitable temperature by means of steam or hot-water pipes.

The mean air-temperature of a stove of this kind is conveniently maintained at about 40–50° C. Whilst too high a temperature is prejudicial to the soap, stove-driers of this type are more economically operated, within limits, at temperatures higher than atmospheric, owing to the rapid increase in vapour tension of water with temperature. The saturation vapour pressure of water at various temperatures is as follows :

°C.								mm. Hg.
10	9·21
15	12·79
25	23·76
40	55·34
50	92·54
60	149·38

It follows, therefore, that a given volume of air at 50° C. can take up far more water than the same volume at 15° C., and accordingly, without proceeding to complete saturation of the air, by working at the higher temperature much less air is required and the cost of heating it is, up to a point, balanced by saving in the power used on the air-blower and in the time taken to dry a given weight of soap.

The amount of drying to be effected varies considerably.

A few varieties of genuine household soap are sold containing 70 per cent. or more of fatty materials, and these may be dried in practice in the liquid state or in stoves. Soaps which have been diluted with liquid fillers ("run soaps") and contain much less fatty material than the genuine soap, are, on the other hand, stove merely in order to harden the outer layers of the bars or tablets sufficiently to render them less sticky.

Again, as already mentioned, soap containing 75 per cent. or more of fatty materials is requisite for *toilet soap stock*, in consequence of the drastic compression and rolling to which it is submitted in the course of "milling" (cf. this section, Chapter III., p. 369). This is almost always carried out, in the larger works at all events, in *continuous driers*, the *Procter* or *Cressonière* machines being in frequent use. Such a plant consists either of a trough, rotating drum, and scraper similar to the margarine drums (p. 303) (for solidifying and shredding liquid soap), or of machinery for first cutting up solid bars of soap and then rolling the chips into thin shreds. In either case the shredded soap then passes on a moving band conveyor through a heated oven and thence on to a further series of rolls at a lower level. These serve further to press out and cut up the partly dried soap, which then passes through a second stage of drying and is then again passed through a final series of rolls, after which it descends through a third heated chamber and is finally cut mechanically into thin shavings suitable for the process of "milling."

The heat is provided, as in the stove-driers, by a current of air drawn by fans over a nest of steam-heated pipes. This stream of hot air is passed through the heating chambers on the counter-current system, *i.e.* it enters where the finally dried soap leaves and passes upwards, so that it finally encounters the soap which has just entered the machine. The time of passage of the soap through the *Procter* or *Cressonière* driers is as a rule about 40–60 minutes, and the temperature and rate of travel of the soap are so adjusted that the dried soap contains 75–78 per cent. of fatty materials.

CHAPTER II.—THE PHYSICAL CHEMISTRY OF SOAPS

SOAPS and soap solutions have proved a singularly interesting and baffling problem to physical chemists for many years, and appear likely to offer a fruitful field for investigation for a long time, since many of the phenomena which they display are by no means fully understood in terms of the current fundamental theories. However, as the result of the labours of a considerable number of investigators during the past twenty-five or thirty years, notably including Spring, Donnan and his co-workers, McBain and his co-workers, and MacLennan, considerable theoretical insight has at length been gained into the physical properties and characteristic behaviour of soap solutions, and also into the physical processes which are in operation in the soap-pan during the critical phases of "graining out," "fitting," and "finishing" a genuine soap.

Possibly, then, this is the most convenient point at which to consider the physical nature of soap during its manufacture and in relation to its subsequent use as a detergent. It is intended here not to give a complete picture or history of the physico-chemical investigations of soap, but rather to select those parts of the studies of various workers which bear more directly upon the technology and uses of soap, so far as can be judged at the time of writing. This may be effected to some extent by first of all considering the mechanism of saponification of fats by aqueous alkali solutions, then by comparing and contrasting the chief physical properties of soaps with those of other electrolytes, and subsequently proceeding to a discussion of the present evidence concerning the physical nature of soaps; the bearing of the physico-chemical data on the chief types of

soap in general use, and on the process of soap boiling and fitting in the pan, will be considered at the same time.

Theory of Aqueous Saponification of Fats.—Until 1932 it was generally supposed that aqueous hydrolysis of fats by caustic alkali solutions was a heterogeneous or two-phase process, that the action took place exclusively at the oil-water interfaces, and that therefore it proceeded the more rapidly the greater the degree of dispersion of the fat globules throughout the aqueous phase. These views were apparently borne out by several features. For instance, addition of soap, free fatty acid, or certain mineral powders, notably finely divided kaolin, promotes the emulsification of fat in dilute alkali and also accelerates the rate of conversion of the fat to soap. Furthermore, different fats have differing capacities for forming emulsions with water, and those which emulsify more readily are saponified, generally speaking, more rapidly.

In 1932 Lester Smith drew attention to the fact that this simple explanation by no means coincides with the whole behaviour of the aqueous saponification process. It was recognized by that date that the earliest stages of the action, whether in the soap pan or by "cold process" (p. 371), are relatively very slow. At a certain point, however, the rate of attack by the alkali increases very greatly and subsequent hydrolysis proceeds at a nearly constant and relatively rapid rate until the process is approaching completion. Lester Smith pointed out that, on the simple theory of action proceeding only at the interfacial areas between fat and water, this sudden increase in rate (which, in the case of saponification of coconut oil at the ordinary temperature is a two hundredfold increase) involves the same increase in the total interfacial area of contact, *i.e.* would connote the comparatively sudden division of each globule, at this particular point in the process, into about 8,000,000 smaller droplets. In other words, this simple physical explanation, if not out of the question, becomes extremely improbable.

Following Pickering's much earlier observation that

many organic compounds are more soluble in soap solutions than in water, Lester Smith demonstrated that fats, as well as caustic soda, are soluble in soap, whether the latter is in aqueous solution or is in the form of either neat or curd soap. He concluded that, after an initial period of slow interfacial reaction, saponification occurs mainly in homogeneous solution in the soap phase. This view accounts for the autocatalytic nature of the reaction, since the medium of the rapid homogeneous action is itself a product of the process. The initial sluggish phase of the saponification (the interfacial phase) can be reduced or eliminated not only by the addition of soap or free fatty acid but also by a small proportion of alcohol, which probably renders the salted-out soap a better solvent for the fat. These views also explain the completeness of saponification by the "cold process." During soap-boiling in the pan, the concentration of electrolyte is usually adjusted so that the soap is present as "neat soap," which in consequence acts as the solvent medium in which most of the fat saponification takes place.

Some Physical Properties of Soap.—So far as soda soaps are concerned, the most striking, but perhaps not the most obvious of their physical characteristics is their sparing solubility at the ordinary temperature: "at room temperatures, all but extremely dilute solutions of all sodium soaps above the caprylate (C_8) are solid." Thus, whilst it is possible to obtain a deci-normal liquid solution of sodium laurate (2·2 per cent.) at 18° , it is not possible to prepare a much more concentrated liquid solution of sodium oleate than N/20 (1·5 per cent.) at this temperature.

At higher temperatures, of course, both sodium and potassium soaps are more freely soluble and ultimately become completely miscible with water, at any rate up to the limits of 64 per cent. of sodium soaps and 40 per cent. of potassium soaps, soaps of this degree of hydration being liquid at the higher temperatures.

Soaps are, however, only characteristic of the alkali salts of the fatty acids over a certain range of the homologous series $C_nH_{2n}O_2$, $C_nH_{2n-2}O_2$, etc., namely, from acids con-

taining about 6 carbon atoms (caproic) up to those containing 20 or 22 carbon atoms (arachidic or behenic acids). Below the C₆ acids the alkaline salts are ordinary crystalline materials with the usual properties of simple electrolytes, and above C₂₂, or already at that point, the solubility of the alkali salts is so slight that for all practical purposes they are insoluble in cold water.

"The appearance, washing power, density and conductivity of the caproates (C₆) distinctly mark the beginning of that deviation from the behaviour of the acetate, which rapidly and regularly increases through the other members of the homologous series until the typical character of the higher soaps is attained. At the top of the scale is behenic acid (C₂₂), often met with in modern soaps and whose soap solutions solidify at a high temperature. The behenates tend to form nearly undissociated colloid and the solutions often have a distinct structure like those of starch. The laurates (C₁₂) are perhaps the most interesting, as they are just in the middle of the series, the lowest really good soap in whose solutions by suitable adjustment of concentrations most of the typical phenomena of the soaps can be produced. . . . Oleic acid (C₁₈ unsaturated) produces soaps *par excellence*" (McBain, 1918).

The chief physical properties of the "true soaps," which distinguish them sharply from ordinary simple electrolytes, are as follows :

Surface Tension.—The surface tension of aqueous solutions of most of the "true soaps" at ordinary temperatures (e.g. 25°) is much less than that of pure water (73 dynes per sq. cm.), and it is to this property that the lathering power of a soap solution is due.

The sodium salts of ordinary oleic acid, linoleic acid, and the highly unsaturated acids of the fish oils lower the surface tension of water so that their solutions only possess a surface tension of about 25 dynes per sq. cm.; next come the sodium salts of lauric, myristic, and palmitic acids, the surface tensions of whose solutions are somewhat higher—25–30 dynes per sq. cm. Soaps containing appreciable proportions

of stearate in addition to palmitate and oleate (*i.e.* tallow) have still higher values, because the saturated stearic acid is beginning to pass, in type, from the "lauric" type of soap to the insoluble colloidal " behenic" type referred to above by McBain. Finally, soaps of solid unsaturated C₁₈ acids ("iso-oleic acids"), such as those present in partially hydrogenated fats, yield solutions with surface tensions above 35 dynes per sq. cm., and the higher saturated acids, such as arachidic, behenic, or lignoceric acids, yield almost insoluble colloidal sodium salts which do not appreciably lower the surface tension of water and possess no lathering power.

These figures refer to solutions at or near room temperatures; at higher temperatures (*e.g.* 60–70°) the solubility of most of the soaps increases considerably, and there is less difference between the physical properties of the various members discussed in the preceding paragraph. It must be borne carefully in mind that surface tension is only an *effect*, and the causes which confer this property (which in its turn confers freedom of lather) remain to be considered.

Viscosity.—The viscosity of soap solutions varies from not much more than that of water to enormous values, forming a perfectly continuous transition from thin fluid, through viscous liquids to a very stiff clear jelly. These changes are not accompanied by any very great change in the electrical conductivity, but above certain limits of concentration the soap changes from a simple colloidal solution into a hydrated liquid crystal or anisotropic phase. The important fact that liquid soaps exist largely in an oriented or "liquid crystal" condition was first established by MacLennan in 1923, and is further considered later in this chapter.

Electrical Conductivity.—Soap solutions possess a much higher conductivity than would be expected if they were made up, like acetates or other lower homologues, of simple molecules of the general formula R.COONa, and they exhibit the peculiar property of a still more abnormal high conductivity in the more concentrated solutions. In the case of

typical soaps the conductivity passes through a minimum at about N/10, and then rises with increase of concentration up to nearly N/1 solutions.

Osmotic Properties.—The osmotic effect is essentially a measure of the amount of crystalloid, as distinct from colloid, matter present in a solution. McBain and his colleagues found that the usual methods of evaluating osmotic pressure by measuring elevation of boiling point or lowering of vapour pressure failed with soap solutions on account of the unavoidable presence of enclosed air, but that depression of the freezing point could be carried out for solutions at 0° C., whilst a dewpoint method was devised for other cases. They found that the osmotic activity was moderately large and that the values obtained were in general about midway between those for simple electrolytes (*e.g.* NaCl) and simple non-electrolytes (*e.g.* cane-sugar). Considered in conjunction with the conductivity results, it appeared that for the "true soaps" the whole of the osmotic activity is required to account for the metal ion alone, and "even that only on the assumption that the negative carrier conducts almost as well as the potassium ion." In very concentrated soap solutions the potassium or sodium ion was found to be the only crystalloidal constituent.

Hydrolysis of Soap Solutions.—It was formerly believed that soaps were hydrolysed in aqueous solution to a very considerable degree, and at one time the detergent power of soap solutions was erroneously believed by some investigators to be due entirely to the alkali set free by the supposed hydrolysis. McBain and his co-workers measured the hydrolysis of many soap solutions by two independent methods which were calculated to afford accurate values without disturbance of the equilibrium of the solution, namely, the potentiometric method and the rate of catalytic decomposition of a compound (nitroso-triacetonamine) by the hydroxyl ion present. It was shown that the greatest hydrolysis present was only equivalent to N/300 alkali, whilst for most solutions it was far less (down to N/3000 or even N/30000). The highest soaps are the most alkaline,

and the alkalinity is less at lower temperatures or in presence of moderate amounts of salt.

In 1921, Beedle and Bolam, working with McBain, gave hydrolysis data for palmitate, oleate, and rosin soaps, and also for commercial soaps prepared from coconut oil and from olive oil, and for trade varieties of genuine household, tallow rosin, toilet, coal tar, cold-process toilet and shaving soaps. The results showed that the hydrolytic alkalinity of all these solutions was much less than had formerly been supposed, and was of the same order as has just been indicated. Incidentally it was established that cold-process soap (*cf.* p. 371) is essentially no more alkaline than boiled soap, and that nut oil soaps (or laurates and palmitates) are less hydrolysed than olive oil soaps (or oleates), the respective figures being about 0.0003N and 0.0007N for the hydroxyl ion concentration of 1 per cent. soap solutions at 90° C.

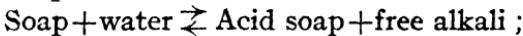
Soaps containing large amounts of nut oils, including cold-process soaps, have a reputation for irritating action on sensitive skins, which was formerly supposed to be due to a greater degree of hydrolysis. The data quoted show, however, that the irritant action must be ascribed to some cause other than hydrolytic alkalinity. Recent systematic tests on the sodium and potassium soaps of pure fatty acids from caprylic to stearic, and on the sodium alkyl sulphates (*cf.* p. 402) of similar molecular range have shown that potassium soaps are more irritating to the skin than sodium soaps, that lauric and myristic acids produce more irritating soaps than other fatty acids, and that, similarly, sodium lauryl sulphate and sodium myristyl sulphate cause much greater irritation than other sodium alkyl sulphates. The effect is thus apparently specific for compounds containing the C₁₂ and C₁₄ acyl chains.

General Theory of the Physical Composition of Soap in Aqueous Solution.—The above illustrations of the properties of dilute soap solutions have been taken mainly from McBain's communications, and are typical of the large mass of careful observations of various properties which have been carried out on numerous sodium and potassium salts

of selected fatty acids, as well as on certain of the mixed soaps as used in practice. For the most part the fatty acids employed were of carefully chosen origin, for example, the lauric and palmitic acids used were of very high purity ; judging from the descriptions given, the oleic acid which was employed may not always have been of the same order of purity as the saturated acids, and it is perhaps not out of place to emphasize once again the urgency of employing no organic compound (especially in the fatty acid series) for physico-chemical measurements of precision unless its individuality and purity are incontestable.

The results of McBain's studies convinced him that soap solutions represented a system in which ordinary electrolytes, colloidal electrolytes, and neutral colloids were in general all present, and that all three classes of solute participated in " true perfectly reversible and reproducible equilibrium." To explain them he adopted the hypothesis that such solutions contain salts in which a simple ion is replaced by an " ionic micelle " (a fatty acid anion combined with an indeterminate but fairly large number of molecules of neutral soap), which exhibits high conductivity and great hydration and which carries a large number of electrical charges. Extensive changes result from alteration in concentration, so that

(i) Great dilution may result in the nearly complete formation of simple electrolyte, together with acid soap as the result of the minor phenomenon of hydrolysis :



(ii) As the concentration increases (*e.g.* from about N/10 upwards) the simple fatty ions rapidly coalesce to form the ionic micelles, until in N/2 or N/1 solution the colloidal electrolyte comprises all the soap, hydrolysis being still more insignificant.

(iii) As the concentration increases still further, the amount of chemically neutral colloid (which, however, is electrically charged) increases still further, and ultimately the stage of " neat " soap is approached, which is further considered below.

In 1922 and 1923 McBain published work on the ultra-filtration and the ionic data of solutions of metallic laurates and oleates which substantiated the general theory outlined above. It was found possible to effect some separation of the ionic micelles from neutral colloid, and it is stated that the ionic micelles are definitely smaller than $15\mu\mu$ and greater than $9\mu\mu$ (*i.e.* the diameter of the ionic micelle is not very many times the length of the laurate or oleate molecule); the neutral colloid consists of much larger particles of size between $75\mu\mu$ and $450\mu\mu$.

This work also led McBain to believe that the neutral colloidal soap exists apart from the ionic micelle electrolyte and not as part of the complex colloidal ion: thus, in a 0.214N solution of sodium oleate at 18° the ionic micelle is present in 0.40N concentration, the remaining 0.174N representing neutral colloid.

Work on the transport numbers (ionic migration) of potassium laurate and oleate confirmed the results obtained by the ultra-filtration method, in showing:

- (i) At very dilute solutions only, the ordinary migration number characteristic of simple electrolytes is observed;
- (ii) In more concentrated solutions the migration of the fatty radical is several times greater than the normal, corresponding to the high mobility of the ionic micelle;
- (iii) The transference values show that most of the chemically neutral colloidal soap is not contained in the ionic micelle, but exists independently as neutral micelle;
- (iv) The hydration of the ionic micelle is apparently about 15-17 molecules of water per unit micelle; nearly all the water present in a normal soap solution is apparently actually combined in hydration of the ionic micelle, the neutral colloid micelle, and the metallic ion.

"The ionic micelle conducts like an ordinary ion of mobility comparable with that of the potassium ion and consisting chiefly of aggregates of fatty ions with hydration of the magnitude of that here assumed. The neutral colloid also moves with the electric current and although it possesses but few charges, so that its conductivity per chemical equi-

valent is almost negligible, nevertheless the conductivity per electrical charge is comparable with that of a slow ion."

More recently, doubt has been thrown on the presence of the neutral colloid particles postulated by McBain, and explanations have been advanced which seem to render this concept unnecessary. G. S. Hartley has shown that the curious changes observed by McBain in the transport numbers with increasing concentration of soap solutions can be equally well explained by the presence, adherent to the ionic micelles, of small ions ("gegenions") of opposite charge to the micelle ions. These gegenions thus partly neutralize the charge of the ionic micelles, and the complex effects resulting from their presence, both on the electrical properties and therefrom on the mobilities of soap solutions, are considered to account for the phenomena ascribed by McBain to the presence of "neutral colloid" particles. Hartley and others also associate the commencement of ionic micelle formation with the point at which the conductivity of the solutions begins to decline, whereas McBain considered that the point of minimum conductivity marked the stage at which ionic micelle formation became notable. It should be added that the more recent theories are based mainly on data derived from the study of long chain sulphate and sulphonate derivatives of the types $R.O.SO_3Na$ and $R.SO_3Na$. Whilst it has been argued that measurements of the physical properties of these compounds are less affected by side actions such as hydrolysis, it is conceivable that there is an essential difference in the behaviour and constitution of dilute solutions of salts of a strong acid (sulphuric or sulphonic) and of those of the very weak higher fatty acids (carboxylic salts, *i.e.* soaps).

Howell has proposed another explanation for the change in conductivity with concentration of soap solutions, namely, that at the point of discontinuity the actual volume of all the anions (*i.e.* hydrated ionic micelles) becomes equal to that of the whole solution. In consequence the solution then consists of a quasi-rigid network of micellar structures which impede the free movements of both anions and cations.

Here, as in Hartley's view, the necessity for postulation of "neutral colloid" aggregates does not arise. It has, however, been suggested by Lawrence that in concentrated solutions the ionic micelles may associate to form loose secondary complexes, and the latter may perhaps be regarded as a transitional stage between the original complex fatty acid anions and the soap fibres which develop in "neat soap" during the cooling operation.

Hartley considers that whilst, perhaps, the ionic micelles initially produced correspond to aggregates of about ten molecules, when nearly all the soap is present as ionic micelles each of the latter may represent an aggregate of as many as fifty molecules. He has also suggested that the interior of an ionic micelle is a mass of hydrocarbon (or, rather, alkyl) chains possessing all the properties of a liquid, and that the capacity of soap solutions to dissolve organic compounds is due to the passage of the solvent into the interior of the ionic micelles. Hartley's conception of the ionic micelle appears to be in harmony with MacLellan's observations on the anisotropic or "liquid crystalline" nature of neat soap (*cf.* p. 362).

The Washing Properties of Soap Solutions.—Many of the necessary attributes of a commercial soap become clearer in the light of the foregoing general theories.

Reference was made above to the older erroneous belief that washing power was due exclusively to the action of free alkali, *i.e.* hydroxyl ions. This was disproved completely by about 1909 by the exhaustive studies of Spring, who demonstrated conclusively that the detergent action of soaps was due to the formation of colloidal absorption compounds. Spring showed that removal of dirt (D) from an object (O) by soap (S) was a process of the type :



both "OD" and "SD" being adsorption compounds, and the active factor in the soap being, according to this worker, "acid soap."

In the light of the present knowledge of soap solutions

it is of course clear that the active components of the detergent solution are not "acid soaps," but one or other form of the complex anions present. Furthermore, later research on detergent action has shown that a number of factors are involved. In the case of a fabric covered with a thin film of adherent oily or greasy matter, the first essential is that the surface shall be wetted with the detergent solution. The low surface tension of such solutions usually confers on them to greater or less degree the property of "wetting out," and the first stage consists in the displacement by the soap solution of the adherent oil films, which collect into minute droplets. The next stage is the removal of these droplets in the form of an emulsion with the detergent solution. In the case of a fabric soiled with dry matter free from oiliness, the same processes may operate, or possibly the action is only one of emulsification, or rather dispersion, of the particles of dry matter in the solution. It is not unnatural, however, that as a rule non-greasy dirt is more difficult to remove by soap solutions than that accompanied by oil films. Impregnation of soiled fabrics with oleic acid before washing with soap solution much facilitates their cleansing; this result led Rayner to suppose that "nascent soap" was more efficient than ordinary soap in solution, but the more probable explanation is that the fatty acid adheres to and penetrates the fibre more thoroughly than soap solution, with the results that, on subsequent application of the latter, the dirt is already either in solution or else adsorbed by the oleic acid, and the above-mentioned processes of wetting and emulsification are more readily effected by the detergent solution.

Again, it should be borne in mind that surface tensions and other properties are just as much *effects*, rather than *causes*, as those characteristics which are described by such terms as "wetting," "emulsifying," "dispersing," etc. The causes of all these phenomena are doubtless largely connected with the presence of the complex micelles which are agreed to be present in detergent solutions by all investigators, whilst the marked orientation of the long-chain salt

molecules is undoubtedly another equally important factor. At an oil-water interface, solute molecules of soap-like compounds, whether simple fatty acid salts or those of sulphuric derivatives of long chain alkyl compounds, take up definite orientation with respect to the two phases, the long alkyl or paraffinoid chain being directed towards the oil whilst the polar (hydrophilic) group or ion is equally attracted towards the aqueous phase. Oriented disposition of the ionic micelles of a detergent solution at the interfaces of the latter with oily or other organic matter must play a predominant role in the mechanism of the removal of dirt from fabrics by detergents.

Apart from these general considerations, it should be noted that a number of specific factors play an important part in dexterity. As already indicated, only a certain range of fatty acids act as "soaps" in the form of their alkali salts; in other words, the non-hydrophilic or alkyl chain must be of a certain length (*ca.* C₁₀) before effective detergent properties are manifested, these reaching a maximum with saturated chains of about C₁₆ or unsaturated chains of about C₁₈. For any one detergent compound, maximum detergent power is reached at a definite concentration of the aqueous solution beyond which no appreciable increase in washing power is observed. Again, a given detergent compound usually has different detergent efficiencies with respect to different surfaces (*e.g.* wool or cotton) which are to be cleansed. These differences can probably also be correlated with differences in surface tension, of penetrability for different fabrics, and of emulsifying or dispersing power in the cases of different detergent compounds. The variations between sodium salts of the different fatty acids in these respects are less significant, perhaps, than between this group as a whole and other detergents such as the sodium alkyl sulphonates, the sodium alkyl sulphates and other of the newer "soapless detergents." Further, the specific differences between, for instance, the sodium sulphates of alcohols of differing molecular weight are frequently more marked than those between

soaps of similar molecular size. Consequently the factors involved in detergent action are numerous, the fabric to be cleansed has to be considered as well as the detergent to be used, and the scientific testing of detergents and detersity is by no means a simple problem.

A word should be added as to the detergent action of the hydroxyl ion, which it is now realized plays an insignificant part in the ordinary use of soap. Nevertheless, especially in cases where a partial hydrolysis may usefully take place during cleansing (*e.g.* removal of grease), it must be conceded that the hydroxyl ion action is to some extent a factor, and it is recognized that the presence of some sodium carbonate, *e.g.* in washing powders, etc., exercises a definite and useful detergent function. In the case of silicated or "run" soaps, the efficiency of the silicate as a detergent is probably due both to the presence of hydroxyl ion and to a somewhat similar colloidal adsorptive action to that exerted by the soap micelles.

The Composition of "Neat" Soap in the Liquid and Solid States.—The work which has been discussed in the preceding part of this chapter indicates that above certain concentrations soaps may exist entirely in the liquid, dissolved, or hydrated condition either as neutral undisassociated colloid or as ionic micellar structures of considerable complexity and size, but beyond this does not elucidate to any great degree the nature of the peculiar changes which take place in the soap pan during the graining out and finishing of a soap charge. MacLennan's study in 1923 of "The microscopic structure of soap" marks an important stage in the explanation of the soap-boiling process and should be read at length. MacLennan showed for the first time that ordinary "neat" soap consists in the liquid state of a mass of "liquid crystals." The occurrence in the liquid state of some kind of molecular structure or orientation (comparable with that of a solid crystal in that it gave rise to the property of rotation of the plane of polarized light, *i.e.* the liquid is anisotropic) had been previously observed by Lehmann and others in certain esters of cholesterol and

some synthetic aromatic compounds (*e.g.* *p*-azoxyphenetole). The presence of a "liquid crystal" structure in a common material prepared to the extent of hundreds of tons per week had not been suspected, however, until MacLennan examined the behaviour of "neat" soap between the crossed nicols of a polarizing microscope: the following typical soap structures were then readily distinguished:

(i) *Solid soap crystals*, encountered only in cases of some pure salts of individual fatty acids.

(ii) *Liquid soap crystals*, strongly anisotropic and giving prominent polarization colour-effects under the microscope; the liquid crystalline soaps are fluid, readily deformable in certain directions, with no definite boundaries, they have not been observed to separate from a mother-liquor, but grow into and through solutions in the manner of an ordinary crystal.

(iii) *Soap fibres*, occurring as rope-like or tangled masses which are feebly anisotropic and which are oriented during growth in a more or less regular fashion. The fibres may develop in and through the liquid crystalline soap (soap-cooling) or may separate from solution (commencement of formation of soap curd).

(iv) *Soap curd*, a mass of soap fibres which enmeshes or entangles, mechanically, a more or less liquid phase. This heterogeneous curd is represented by a freshly grained-out soap curd, or by a cold nigre, but it should be noted that a finished technical "curd soap" is not a soap curd within this definition, but a "neat" soap of somewhat open finish (*cf.* p. 342).

(v) *Soap Gels*.—Optically inactive or isotropic jellies containing no liquid crystalline structure. These are rarely to be encountered in soaps, except in the case of perfect solid transparent soaps from alcohol, or in commercial soft soaps, which consist of a mixture of drops of "liquid crystal" anisotropic fluid embedded in an isotropic jelly or "soap gel."

(vi) *Soap Solutions*.—Solutions from which any anisotropic microscopic appearance is absent and containing more dilute soap than the preceding (*e.g.* freshly saponified dilute soap before graining out, hot nigre or hot soap lyes).

MacLennan's observations of the changes in the microscopic structure of soap during manufacture are sufficiently interesting to be briefly summarized : The appearance of small samples withdrawn on hot slides varied greatly, as would be expected, with the progress of the charge. Molten fat could readily be detected in the earlier stages, while part, at any rate, of the soap floated around as much larger globules of highly anisotropic liquid crystal. On completion of saponification the picture was one of fluid crystalline globules floating in a more or less concentrated aqueous solution of soap. The first product of saponification was always seen to be a fluid crystal, but soap fibres were also sometimes observed to be present, presumably when the alkali was concentrated or had not been taken up by the fat. On the other hand, on occasion with dilute boils the soap was entirely in solution at 100° C.

On graining out with salt, microscopic observation revealed a remarkable series of changes taking place in the soap-charge : the soap, when fully grained out and ready to separate to the surface, always existed mainly as tangled masses of soap fibres from which the lye was ready to drop as soon as the system came to rest. Conversion into the liquid crystalline form could not be observed whilst salt was present in any quantity, but, as soon as the lye settled, a partial conversion into crystalline fluid followed in the surface soap.

After fitting and finishing, the upper layer of neat soap was always found to be predominantly a crystalline fluid at soap-pan temperatures. The nigre presented a marked contrast—it was normally isotropic or " optically empty " at the temperature of the pan, but on cooling " flashed over directly into a dead-white opaque mass, having the general characteristics of a heterogeneous curd. A crystalline fluid stage did not precede fibre formation." Although the nigre soap fibres were but feebly anisotropic they passed into a crystalline fluid by getting rid of enmeshed brine and heating, thus behaving exactly like a true curd of a pure soap.

Thus the whole soap-boiling process "turns on the alternation between soap in the fibrous and in the fluid crystal condition. Solutions play a minor part during saponification in nigre and soap lyes, whilst soap curds, as defined scientifically, occur only in the grained soap and the cold nigre."

Before proceeding to MacLennan's account of the soap-cooling process and his examination of commercial soaps, reference may be made to McBain's study of the phases and equilibria underlying the soap-boiling processes (1925). Following up MacLennan's observations, it was established that the fluid crystalline (anisotropic) and ordinary (isotropic) soap solutions constituted separate immiscible phases, and that a second anisotropic and previously undetected fluid crystalline soap, termed by McBain "middle soap," was capable of existence in medium concentrations. All the soap-boiling operations were shown to depend on equilibria between the possible phases present.

Studies of the system sodium palmitate—sodium chloride—water at varying temperatures and concentrations showed the existence of seven possible stable two-component systems, whilst it is also stated that as a first and close approximation the complex fatty contents of a fat-charge will behave like the simple three-component system studied (apart from the separation of solid crystalline phases). The seven fields in which two phases each of varying composition can co-exist are :

- A. "*Middle soap*" and *isotropic solution*—not definitely recognized in practice.
- B. "*Middle soap*" and "*neat soap*"—not definitely recognized in practice.
- C. "*Neat soap*" and *curd fibres*—not normally present in the pan, but occurring during soap cooling in frames (*v. infra*).
- D. "*Neat soap*" and *isotropic solution (nigre)*—the normal state of affairs in the pan during "fitting."
- E. "*Neat soap*" and *isotropic solution (lye)*—the normal condition during graining out with salt, but just prior to the actual formation of soap curd (field G).
- F. *Nigre and lye*—a small region, not often encountered during the soap-boiling process, in which isotropic solution can separate into these two phases.
- G. *Soap curd and isotropic solution (lye)*—the normal condition of a soap charge which has been fully grained out.

This paper, as well as MacLennan's, should be read in the original in order to obtain the full details of the investigations ; it can only be added here that the complete phase-rule analysis of the contents of the soap pan supplies theoretical backing for the practical art which has been evolved in the course of generations by the soapboiler, and it may be hoped that in due course still further precision may be arrived at in the art by attention to the results now disclosed by the " academic " investigations. The unfortunate fact that, as so often happens, physical chemistry has been outstripped by " rule of thumb " for many years in the soap pan should not deter the technical operator from invoking its assistance when at length it has developed a consistent and sound theoretical treatment which satisfies all the known facts.

It may be observed that the work of MacLennan and McBain disposes at once of the age-long controversy as to whether the 64 per cent. " genuine " sodium soaps and the 40 per cent. " genuine " potassium soaps contain the water which is present in the form of " chemically combined " or " mechanically held " water of hydration. It is now evident, from phase-rule considerations, that the composition of the " neat soap " as it separates in the fluid crystalline condition is controlled solely by the pressure of the system in which it is produced : so that, as regards the final bar or toilet soap, " although its total composition is necessarily that of the original sample of ' neat soap,' its constitution and structure have nothing to do with those of ' neat soap.' " In the process of cooling the " neat " soap one of the variables—temperature—has been altered and consequently the composition of the soap changes into the two-phase system " neat soap " and " soap fibres." The bar of soap is thus a heterogeneous mixture, necessarily of the same total composition as the original " neat soap," but consisting of innumerable hydrated soap fibres enmeshing solid solutions of the more soluble soaps.

The older views of Chevreul, supported by Lewkowitsch, that the water present in a finished " genuine " soap is

"water of constitution," therefore go by the board, whilst those of Merklen, who indulged in a somewhat prolonged polemical discussion with Lewkowitsch and held that the water present is adsorbed by the soap, are also seen to be not wholly accurate.

At the same time it is fair to add that Merklen (1907) made the first attempt to apply the phase rule to the process of soap-boiling, albeit only in respect to the two systems D and E (above), *i.e.* "neat soap" and "nigre," and "neat soap" and "lye."

Soap Cooling.—We may return to MacLennan's paper for useful information on the setting and solidification of the fluid crystalline "neat soap." When the latter was allowed to cool very slowly, as in the frames, soap fibres gradually grew into and through the fluid crystal mass in a symmetrical and oriented fashion, whilst the fluid crystals themselves took on a certain amount of solidity and rigidity. "Slow cooling permitted of maximum orientation, both of crystals and fibres. In sections of such soap a distinct optical axis existed and caused the section as a whole to extinguish on rotation between crossed nicols. Old thoroughly matured soaps, which have in the first instance been slowly cooled and neither milled nor plodded, have been found repeatedly to be highly anisotropic. . . . The internal orientation of structure which soap on slow cooling can develop is visible externally to the unaided eye in 'feather' and in the silky sheen or even opalescence which such soaps frequently show." Rapid cooling of the viscous "neat soap" was invariably observed, on the contrary, to permit of practically no orientation in structure. Much of the original fluid crystal was found to persist as more or less solid irregular lumps, but the whole soap was permeated with very fine and very irregular fibres. The objections which have been raised to soap cooled by rapid mechanical coolers instead of in frames, on the score of "inferior quality," are thus seen to rest on a very sound basis: in order to obtain the most perfect structure in a solid bar of soap it is undoubtedly necessary for the rate of cooling to be as slow as possible.

Reference may be made in conclusion to the typical appearance of various kinds of commercial soaps under the polarizing microscope, as described by MacLennan :

Genuine household soaps showed, in spite of individual variations, a mixture of solid crystalline fragments with a mass of more or less symmetrically oriented fibres.

On heating the soap sections, the fibres were found to disappear at about 60–90° C., the soap becoming strongly anisotropic (fluid crystalline matter present) at 80–100° C.

“*Filled*” soaps, including mottled soaps, resembled the genuine soaps if little silicate was present, but in larger proportions the latter appeared, with soap fibres, to act as a flux for enmeshed spherical globules of solidified crystalline soap.

Commercial transparent soaps, made by evaporation of alcoholic solutions, were found to be quite isotropic and devoid of crystalline structure ; they appeared to consist essentially of solidified soap gel.

Commercial soft soaps consisted as a rule of fluid crystal globules embedded in a matrix of isotropic substance ; occasionally, in less perfect specimens, there was a tendency to some fibre formation, whilst “figging” (the occurrence of small granular patches in soft soaps) was readily shown to be a definite separation of some solid constituent of the mixture.

The original should be consulted for further very informative descriptions of the structure of the individual soda soaps of stearic, palmitic, lauric, caprylic, oleic, and elaidic acids.

Any account of the physical side of the complex problems associated with soaps in their manufacture and application is bound to be somewhat discursive, but it is believed that the matter in this chapter may afford a general glimpse of the present state of the theoretical knowledge of the subject ; space forbids any more detailed treatment.

CHAPTER III.—THE PRODUCTION OF TOILET AND SHAVING SOAPS

The Fat Basis of Toilet and Shaving Soaps.—The qualities required in these soaps are primarily good solubility and free lathering power, and the fat charges employed are chosen mainly in order to fulfil these essentials.

Most of the best quality toilet soap in use in this country is based on a mixture of nut oils and best tallows : in former years the base consisted almost exclusively of best coconut oil with beef tallow, whilst at a later stage palm kernel oil was used in partial or complete substitution of the coconut oil, and mutton tallow in place of the softer beef tallow, any excessive hardness due to this tallow being compensated for by the presence of a small quantity of a soft fat, usually cottonseed oil.

The actual fat charges employed at the present day vary widely within certain limits, but the essential constituents in most cases are still nut oils and tallows. Minor proportions of other oils are employed in order to meet the economic factors of the raw material markets ; thus groundnut or partially hydrogenated cottonseed, soya bean, maize, or whale oil have found some use in toilet soap manufacture.

Since it has become possible to obtain bleached palm oil of excellent colour, this material (which contains palmitic and oleic acids in large quantities and is therefore well suited for toilet soap) has been widely used in place of the more expensive nut oils and tallows. Palm oil soaps are frequently used without addition of any animal fats to the charge, a proportion of cottonseed, olive, or other liquid fat being desirable in order to obtain the best texture and lathering power.

Finally, castor oil is employed in some transparent soaps

in order to increase the clearness and brightness of the soap tablet, although it has detergent powers of a low order.

The soaps employed in shaving sticks, powders, and creams present as a rule some differences from the average toilet tablets. They require to be fairly hard in texture (for shaving sticks) and at the same time to be freely soluble and to develop a very rich lather. This is mainly secured by the use of a mixture of potash and soda soaps, and a shaving soap charge is therefore prepared by means of a mixture of caustic potash and soda instead of the latter alone, or by caustic potash alone followed by graining out with brine, as a result of which a mixture of potash and soda is left combined with the fatty acids. The fat charge for a shaving soap is therefore generally saponified by itself, and consists as a rule of a mixed nut oil and soft tallow base.

The actual cost of the fat employed in toilet soaps should not be so serious a consideration as in the cheaper kinds of soap, because the final price of the soap as sold permits a far wider margin in this respect than in the case of household, textile, and similar soaps.

Manufacture of Toilet Soap from the Pan.—The fat charge, after selection on the lines indicated above, is saponified and the resulting soap washed in the pan as described on p. 284. After framing, barring, and stacking, the long bars of soap are machine-cut into shavings and dried in stoves, or more generally in a drier of the Procter or Cressonière continuous type as described in Chapter I. The dried scraps of soap, now containing 75-78 per cent. of fatty materials, are fed into "milling" machines, which consist of heavy rollers between which the soap is crushed and pressed out into very thin, scale-like shavings. The milling process, the primary function of which is to re-work and mould the soap so as to secure complete homogeneity of texture, serves equally well for the incorporation of colouring matters, perfumes, and sometimes other accessories such as lysol, glycerine, or medicaments of other kinds and, in the case of low-grade toilet soaps, of "fillers" such as casein, flour, dextrin, sugar, and the like.

Needless to say, the characteristic colour and perfume associated with a given toilet soap are as little a function of its fatty composition as the brand stamped on the finished tablets, and the various colouring matters and perfumes which may be employed cannot be discussed within the scope of this work. The golden, cream, green, mauve, or other hue of the finished tablet is due to small proportions of selected dyestuffs, generally coal-tar colours, which are added in alcoholic or aqueous solution. The perfumes are blended from synthetic or natural sources by specialists in such a manner as to confer the odour which is to be typical of the particular brand of soap, and are also added to the shredded soap in the milling machine in alcoholic solution in small, exactly prescribed proportions. The production of the perfumes employed, whether natural or synthetic, is an industry of considerable proportions, which is usually conducted separately from the soap factories and which is obviously not directly connected with the subject of fatty oils.

In some soaps glycerine is also added at this stage to increase the translucent appearance of the finished tablet, and for another variety of soap—*superfatted toilet soaps*—a small percentage of pure neutral oil (palm kernel or coconut oil, lanolin or olive or groundnut oils) is added, the purpose of which is to absorb the last traces of any free alkali in the soap and leave a slight excess of neutral fat in the final tablet.

Medicated toilet soaps containing carbolic acid, sulphur, petroleum, or other material intended to serve a specific medical purpose—antiseptic or otherwise—are produced at the same stage of the general process by adding the appropriate pharmaceutical materials with perfume, colouring matter, etc., to the shredded soap in the milling machine.

The shredded soap is then milled for some time and is frequently then re-worked in a second mill; the milling process is carried out in a room the temperature of which is about 15–20° C., so that, whilst the soap is sufficiently plastic to be worked readily, it is not sufficiently hot to be sticky nor to cause the somewhat delicate perfumes or dyestuffs employed to be affected deleteriously.

After milling, the fine shavings of soap pass on to a "plodder," in which they are rammed together by an Archimedean screw and pressed through a perforated plate into a conical nozzle, finally emerging through dies of various shapes according to the shape and size intended for the finished tablets. The prepared toilet soap is thus converted into cylindrical or rectangular bars, which are mechanically cut into suitable lengths for the tabletting or stamping machines.

Brands of soap which are sold in a fundamentally rectangular form (usually with rounded edges) are moulded in rectangular bars, whilst the more oval or ovoid shapes of tablets, which are popular at the present day, are stamped from cylindrical bars 3 or 4 inches in diameter, as the case may be; shaving sticks are moulded in cylindrical rods of the exact diameter of the finished article and only require cutting and wrapping.

The stamping process, or conversion of the plodded bars into tablets, branded by means of dies, is effected in modern factories by special machinery which converts the bars into finished, moulded tablets, stamped with the ornamental brand of the particular type, in one operation; the residual soap which is cut from the tablets or loose edges in this process is re-plodded with fresh milled soap. The soap is then ready for wrapping and packing (usually nowadays in one and the same machine) in a more or less attractive guise, according to the quality of the article.

Manufacture of Soap by Cold Process.—"Cold-process soaps" are made, without boiling the fats in a pan and without the application of any heat other than that required to melt fats originally solid, by producing an intimate emulsion in a crutching machine of the melted fat with exactly the correct amount of caustic soda requisite for saponification. The process proceeds in the cold when the emulsion is left to stand, and after two to four days soap formation is complete and the mass is ready for cutting into bars and tablets.

The cheapness and simplicity of this process rendered it

very attractive to former generations of soap manufacturers, who operated as a rule on a very small scale ; in those days coconut oil, the oil most suitable for this process, was relatively cheap and glycerine recovery was not troubled about. On the other hand, the soapmakers in question were mainly devotees of "rule of thumb" and were not too particular about the quantity of alkali used, with the consequence that the products were sometimes incompletely saponified and heterogeneous, or else contained an excess of free alkali. As a result the "cold-process" method fell into disrepute, but it is coming back into favour to a certain extent, since modern scientific control renders it quite possible to produce good quality toilet soap base by this means, free from alkali or excessive fat, and of approximately the same composition as an ordinary "fitted" soap from the pan. The only difference, and one which enhances the appearance and quality of the soap rather than otherwise, is the presence in the finished article of the glycerine liberated during saponification ; this is of course not recoverable as glycerine, and therefore the application of the "cold process" depends to some extent on the state of the glycerine market.

The necessary emulsification is only produced readily in the cases of soaps of the fatty acids of relatively low molecular weight or of ricinoleic acid, *i.e.* of soaps derived from the nut oils or from castor oil ; this is probably due to the specific interfacial surface tensions of the various glycerides with the caustic soda solution employed.

However, when the correct degree of stable emulsion is secured, the contact between caustic soda solution and fat globules is so intimate that saponification proceeds steadily at the ordinary temperature, or strictly speaking somewhat above it, owing to the development of a certain amount of heat by the interaction of base and glyceride. Further, the fats which contain larger proportions of stearic, oleic, and linoleic acids can also be brought into the requisite state of emulsion if nut oil or castor oil is present and a higher temperature is employed during the preliminary crutching process.

The actual conditions for a given fat charge are determined by its composition, and the temperature of crutching or emulsification and the strength of the caustic soda solution are adjusted to suit the particular case ; as in soap-boiling, the correct conditioning of the emulsified mass is somewhat of an art which can only be acquired by actual and continued practice.

✓Broadly speaking, the mixture of coconut or palm kernel oil with the appropriate quality of tallow and/or soft oils of the cottonseed oil type, is run into the crutching machine concurrently with the correct amount of caustic soda solution (of about 60-75° Twaddell according to circumstances), thoroughly agitated at the most suitable temperature (usually between 40 and 60° C.) until complete emulsification is reached, and then left standing (the vessel being covered to conserve the developed heat) for about four days. The saponification is usually finished in about 48 hours, and after cooling for a further day or so the solid soap is removed and cut into bars. In order to facilitate the latter purpose the crutcher may be made in a rectangular shape with frame sides which can be detached at the conclusion of the process.

The subsequent drying and working of the soap base is the same as of that made by the boiling process.

“**Re-melted Soaps.**”—A somewhat old-fashioned method of producing toilet soaps which may still find some use in small establishments is that of taking a finished curd soap and heating it or “re-working” it in vessels heated by dry steam coils or jacket. The soap concentrates, of course, to some extent owing to evaporation of water, and at the same time any free caustic soda is converted to carbonate by the action of atmospheric carbon dioxide. Towards the end of the re-working or re-melting, colours and perfumes may be added, after which the soap may be run into frames as in the case of household soap, which it resembles in type rather than the modern forms of toilet soap of high fatty material content with delicate colour and odour.

The Chief Varieties of Best Quality Toilet Soaps.—
The high-class soaps include a number of distinct varieties

designed to serve special purposes, the chief classes being as follows :

Ordinary Toilet Soap.—This is made as described on pp. 369-371, and consists essentially of a coloured and perfumed soap base, the latter consisting of genuine milled soap containing 75-78 per cent. of fatty materials combined with soda as base, and free from any caustic alkali.

The composition of the fat base may be either a mixture of nut oils and tallow, with or without a soft oil such as cottonseed oil ; or practically exclusively nut oils ; or nut oils, tallow, and/or hydrogenated cottonseed, whale, soya bean, etc., oils ; or palm oil and tallow ; or palm oil with a soft (liquid) vegetable oil ; or a number of other possible mixtures of the common high-grade technical fats, according to the texture desired and the ruling prices of the raw fats to be employed.

Superfatted and Glycerine Soaps.—In order to remove all traces of harsh action and to increase the emollient effect on the skin, small quantities of neutral fat or glycerine are added to some toilet soaps.

Soaps in which unsaponified fat is deliberately allowed to be present are termed "*superfatted*." The fat may be of the same type as that in the original soap base or one of the constituents thereof, in which case it may be added at the close of the "strengthening change" when the soap is "finished" in the pan (p. 340). In *superfatted toilet soaps* the addition is more usually made at the milling stage, together with perfumes and colouring matter, and in these cases the material used is more frequently a high-grade soft oil such as olive oil or groundnut oil, or refined lanolin (from wool grease) of the highest quality.

Glycerine is similarly added in other cases in the milling process for the same purpose, namely, in order to improve the "feel" and emollient action of the soap on the skin.

Cold-process soaps, of course, contain glycerine from the hydrolysed fats and are also frequently prepared with a slight excess of fat over caustic soda, so that in such instances they are also superfatted.

Transparent Soaps.—There is a considerable demand for toilet soaps which are translucent and clear in appearance as distinct from the ordinary opaque tablet, and this is met mainly by dissolving the “ milled ” soap (in the fine shredded form before “ plodding ”) in alcohol and settling the warm solution. Certain impurities, including small quantities of sodium chloride and carbonate, separate at this stage, and the clear solution is drawn off, the bulk of the alcohol evaporated and condensed for further use, and the concentrated alcoholic solution is run into shallow frames. After standing until firm the blocks of soap are placed on trays in a stove and exposed to a current of air at about 30–35° C., which removes most of the remaining alcohol ; the entrained alcohol vapour is recovered by passage through a refrigerated condenser, or better, by scrubbing the emergent air through water and fractionating the scrubber liquor.

In addition to the alcohol process, other means of securing more or less transparency are as follows :

Cold-process soaps, if made from nut oils alone, are of a semi-transparent nature, the latter being intensified if additional glycerine is added to the cold-process charge ;

In cheaper transparent toilet soaps it may be found that the translucent effect has been secured by somewhat large additions of sugar, glycerine, etc. ; these are not, however, to be classed with high-grade toilet soaps.

Floating and Marine Soaps.—In order to produce a soap which will float on the surface of water a cold-process soap, or a milled and plodded soap, may be violently agitated or injected with air after being brought into a warm, pasty condition, and then allowed to cool and set in moulds ; the solidified soap retains the air in the form of enclosed minute bubbles and the specific gravity of the whole is less than that of water, the product being sold as *floating soap*.

Marine soaps are designed for use with sea-water, e.g. on ocean liners, and consist essentially of soap from coconut or palm kernel fat. These soaps, containing very large proportions of sodium laurate and myristate, are much less

readily "salted out" by brine than soaps of fatty acids of higher molecular weight (a point which obviously concerns the amount of salt required to "grain out" soaps from fats of varying types in the soap-boiling process, p. 339). Consequently pure nut oil soaps are made to some extent for use on ships, and the lathering properties in salt water may be increased still further by the use of potash-soda mixtures in place of soda alone, or by addition of rosin.

Lower Qualities of Toilet Soap.—It is hard to say where low quality in toilet soaps commences and high quality terminates, except that the highest grade is that represented by an artistically coloured and perfumed soap made from a base of nut oils and best tallow.

Whilst, in comparison with the latter, cold-process, transparent, glycerine, and (especially) rosined soaps must be considered as somewhat inferior, they are still of good quality as regards content of fatty material compared with the very cheap toilet soaps which, as a rule, contain much less than 60 per cent. of fatty material.

These are made in a variety of ways by "filling" the soap at the milling or crutching stage with large proportions of sugar, starch, or dextrin solutions, all of which contribute to a transparent finish; or by incorporating mineral oil or hydrocarbon products such as tetralin; or solid "fillers" such as rice, flour, talc powder, or similar materials.

The heavily rosined soaps and hydrocarbon soaps are not lacking in fair detergent and lathering properties, but the other types mentioned are merely soaps "filled" with at best inert material in order to make it possible to supply the product at the low prices fetched by soaps of this class. At the present day the bulk of the demand is satisfied by the genuine toilet soaps of the different varieties which were described above.

Shaving Soap.—Material for shaving purposes is sold in at least three forms:

- (a) Solid blocks of soap;
- (b) Soap powders;
- (c) Emulsified or semi-liquid pastes.

The solid blocks, or shaving sticks, have already received mention (p. 369), their manufacture being similar to that of best toilet soap, whilst they are usually composed of a nut oil-tallow base combined with a mixture of potash and soda, in order to favour the production of rapid and abundant lather from a small film of soap.

Powdered shaving soap consists of a similar material which is dried further than is usual for toilet soap, namely, until it contains 85 per cent. of fatty materials, and is then milled and ground to a fine powder. It has also been suggested to crutch the soap base after framing, and then spray the liquid soap by means of a current of compressed air through a fine jet into a chamber ; the "atomized" drops of soap solidify before reaching the floor of the chamber and form a fine powder.

Finally, a number of shaving materials are in the form of liquid pastes contained in tubes ; these are proprietary articles of various types and consist of either

(i) An emulsion of shaving soap of the type first described with neutral fats or soft waxes or high-grade petroleum oil, glycerine, or the like material ; this is applied by rubbing and the addition of water and formation of lather is unnecessary ; or

(ii) A shaving soap of reduced fatty acid content, manipulated so as to produce a cream, used by producing a free lather in the usual way with a moistened brush ; or

(iii) Many modern shaving creams, for application by hand without brush, include instead of, or in addition to, ordinary soaps fatty acid salts of triethanolamine (p. 404), or sometimes sodium higher alkyl sulphates (p. 402), mixed with, for example, lanolin, glycerol, or high-grade liquid paraffin (or more than one of these) to form a smooth creamy emulsion.

CHAPTER IV.—THE PRODUCTION OF HOUSE-HOLD SOAPS

THE great variety of household bar or tablet soaps which are on the market can be grouped into the following classes :

(i) *Genuine household soaps*, in which the soap is substantially in the condition in which it has been "cleansed" from the pan, except for the presence of colouring and perfuming materials; such soaps may be entirely fatty, i.e. containing substantially nothing but fatty acid sodium salts and not more than 30 per cent. of water, or may be rosined soaps, that is, fatty soaps with which a certain minor proportion of rosin soap has been incorporated. The latter soaps are embraced in the term "genuine" soaps. Genuine soaps can usually be identified by their characteristic "feathered" structure.

(ii) "*Run*" soaps of two different types (*v. infra*), in which the proportion of true soap present has been reduced to a smaller or larger extent by incorporation of sodium silicate or carbonate solution with a genuine soap, followed by a process which hardens the resulting soap sufficiently to permit the bars to retain their shape.

(iii) *Mottled soaps*, which may be produced either from "genuine" or "run" soaps, but at the present day are made to a preponderating extent from the latter form.

(iv) "*Filled*" soaps, which are not only "run" with sodium silicate or carbonate solution, but contain in addition solid inert substances of an almost or completely non-detergent character. This class represents the lowest grade of household soap and is definitely much inferior in detergent power to either the "genuine" or "run" soaps.

(v) Special classes of household soap, such as carbolic or naphtha soaps.

Genuine Household Soaps.—Little, if any, “genuine soap” from which rosin is absent is ever found in commerce at the present time. The best household soaps almost invariably contain a certain proportion of added rosin soap, which is, however, not to be regarded as an adulterant, since it improves the lathering power of the soap and also contributes to its fresh, bright appearance and confers a faint, pleasant odour upon the finished material.

The rosin employed is obtained from American, French, or Scandinavian pines and consists of a solidified exudation of more or less transparent appearance, the colour varying from very pale yellow through many shades of brown to almost black. The rosin imported to this country amounts to about 70,000–75,000 tons per annum, of which over a third is utilized in soap; it is graded and sold according to colour, the palest kinds being graded “WW” and successively darker qualities being given other letterings which have a definite significance in the trade.

Chemically speaking, rosin consists almost exclusively of complex terpene acids (chiefly abietic and pimaric) of high molecular weight (about 325) or of the corresponding acid anhydrides, together with small proportions of gum-like or resinous material and mechanical impurities such as vegetable fibre, twigs, etc., of a cellulose character. The rosin acids and anhydrides combine readily with soda (in the form either of sodium carbonate or caustic soda solution) on gentle boiling, and if the rosin is broken up and boiled in a simple type of soap pan with the calculated amount of sodium carbonate solution, a solution of *rosin soap* results which, on addition of brine in the ordinary way, may be “grained out” as in the case of a fatty soap, but with this difference, that the separated liquid rosin soap is heavier than the lye and settles to the bottom of the pan, leaving the lye on the top. The *rosin soap* so produced may be run off and is used *per se* to a small extent as a kind of soft soap; this must not be confused with the *rosined* (household) *soaps*, which consist of a fatty soap mixed with a subsidiary proportion of rosin soap.

The proportion of rosin to fat in genuine household rosined soaps is often about 1 : 10, and is rarely allowed to rise above 1 : 3. In many establishments the rosin is merely crushed by hand and shovelled direct into the soap-charge during saponification in the pan, in others it is the custom to make up the rosin soap separately in a smaller subsidiary pan or pans, the rosin being crushed on a grid framework through which it passes in fragments of suitable size *via* a chute into the pan at a lower level. In this pan the rosin is boiled with carbonate solution and grained out with brine, and the lower layer of liquid rosin soap is pumped into the main soap charge after the first or second brine wash (*cf.* Chapter I., p. 340).

Genuine rosined soaps are crutched with colour, perfume, etc., as desired, framed and barred as described on pp. 342-344.

"Run" Soaps.—“Run” soaps must be further subdivided into two definite grades :

(i) Soaps “run” with very concentrated liquor and in which the fatty acid content is still between 50 and 60 per cent., usually 55-58 per cent.

(ii) Heavily liquored soaps, in which the proportion of true soap has been considerably reduced by addition of relatively weak solutions of sodium silicate, carbonate, chloride, etc. The best of these soaps contain about 45-48 per cent. fatty materials, but this is reduced in other cases far below this limit.

(i) In the first type, the finished soap from the pan is introduced into the crutchers and mixed, not only with colouring matter, etc., but with sufficient 140° Twaddell alkaline silicate, 75° Tw. neutral silicate, or saturated (64° Tw.) carbonate solution to reduce the fatty material content to about 55-58 per cent.

(ii) The second grade, which still possesses good detergent and lathering powers, but contains much less fatty materials, is produced from genuine rosined soaps (but often made from fats of inferior quality to those employed in the best grade household soaps) by incorporating more dilute solutions (*e.g.* from 40° to 15° Tw.) of silicate and/or carbonate.

When complete homogeneity has been reached, the soap is framed as before, and then cut up into bars as usual. Owing to the increased water content the bars are, however, somewhat sticky, and they are therefore stoved for a brief period to form a relatively dry, hard film on their surfaces.

The addition of sodium carbonate or silicate to soap has been much criticized from time to time, but the practice can hardly be regarded as in any sense an adulteration, since it consists, quite openly, in the partial replacement of fatty acid by a cheaper mineral acid, the sodium salt of which has certain useful qualities in conjunction with soap ; such soaps are usually retailed at considerably lower prices than the 63 per cent. fatty material or "genuine" household soaps, so that the consumer is not in any way asked to pay for fatty matter which is not present.

The part played by sodium carbonate and sodium silicate is twofold : on the one hand water-softening is promoted by conversion of soluble calcium salts in the water into calcium carbonate or silicate, and on the other hand, according to the present concensus of opinion, either compound has a definite value as a detergent. The caustic alkalinity of a silicate solution containing two or more molecules of silica per molecule of combined soda is no greater than that of a similar solution of sodium carbonate, and is progressively less as the proportion of silica in the silicate is increased. Solutions of sodium silicate are colloidal in nature, and in this respect are similar to soap solutions and exhibit the same qualities of removing dirt and greasy matter, whilst carbonate solutions also possess distinct dirt-removing powers.

"Run" soaps are therefore good cleansing materials for ordinary purposes ; it has been suggested that their use in washing textile goods is harmful owing to deposition of silica in the fibre of the material, but again this is hardly likely to occur, unless excessively silicated soaps are employed and insufficiently rinsed out. The silicate present in a soap which has been "run," say, to a content of 45 per

cent. fatty materials could not cause deposition of silica except by very incorrect and abnormal conditions of usage.

Mottled Soaps.—Present-day mottled soaps are almost invariably “run” soaps containing silicate and about 45 per cent. of fatty acids, but their employment was originally due to a belief that “mottled” appearance was inconsistent with the presence of less than about 60 per cent. of fatty materials.

The history of the development of the mottled soap trade is briefly as follows :

If slightly coloured fats be used in the manufacture of a “genuine” soap and the latter is “finished” in the pan as a fairly open-grained curd (*cf.* p. 342) instead of being completely closed, the final soap is, strictly speaking, a two-phase system of true soap and a soap solution resembling a very pale “nigre” (but in a concentrated form and of the same density as the true soap). On cooling, the small amount of impurities tends to concentrate in the latter phase, and the cold soap thus shows a marbled or veined appearance (“mottle”). If a mineral colouring matter such as ultramarine or Prussian Blue is added, this also passes completely, if the soap is correctly manipulated, into the “mottle,” and the result is a soap containing irregular blue-coloured “marbling” or veins distributed throughout the mass.

It was originally believed that this “mottled” effect could only be produced in an almost “genuine” soap, *i.e.* one containing about 60 per cent. or more of fatty materials, and this created a popular demand for mottled soap which still persists in spite of the fact that, as already stated, most of the mottled soap now sold is a “run” soap containing only about 45–50 per cent. of fatty materials.

In the present-day procedure, a “genuine” soap base is prepared from fats of reasonably good quality and “liquored” with silicate solution, as described in the foregoing pages, to 45–48 per cent. fatty acid content. It is then pumped into a clean soap pan and got into condition for mottling by a repetition of the boiling process. The

actual mottling operation is a very delicate one, inasmuch as the two phases referred to must be in exactly the correct physical conditions (equal density and other factors are probably concerned); otherwise the "mottle" does not "strike," *i.e.* the more or less homogeneous veining is replaced by a mass of clear soap resting on the "mottle" which sinks as a kind of "nigre" to the bottom of the pan, or may be distributed in small indistinct grains throughout the whole mass without definite veining.

The adjustment of the soap solution to the exact point at which the mottling will take place evenly is a matter of skilled technique, which is even more dependent on the art of the soap-boiler than the graining-out and finishing processes of genuine soap. The manipulator is guided mainly by practical experience and by the manner in which a sample of the boiled soap sets on a testing ladle. The soap sample should set moderately slowly and then present a dull, somewhat frosted appearance when ready for the addition of the blue mineral colour; at this point it usually contains somewhat less than 1 per cent. of sodium chloride.

After addition of the mineral colour with sufficient boiling to incorporate it evenly, the soap is transferred to the cooling frames as quickly and as hot as possible. The frames for mottled soap are lagged so that the cooling process takes place much more slowly than for ordinary soap and are kept in a moderately warm room, where they are left undisturbed for a week or ten days.

The framed soap is cut into bars and these are immersed ("pickled") in cages in a tank of brine, the liquor preferably containing about 1 per cent. of a 10 per cent. solution of sodium hypochlorite. As in the case of other "run" soaps, this procedure hardens the bars and makes them sufficiently rigid for handling in the retail trade.

"Filled" Soaps.—There remains the lowest grade of household soaps, which in good modern practice only represents the final by-product, as it were, from the better-class soaps, and consists of residual soap material of poor quality which is made up into a cheap soap by "running"

with silicate or carbonate and in addition incorporating in the soap, by crutting, solid inert materials such as clay, chalk, talc, or meal.

Soaps can be made by judicious blending with "fillers" so that a more or less rigid tablet results which may contain less than 20 per cent. of fatty material, and at one time the production of such soaps by small makers was practised on a somewhat lucrative scale, as little distinction as possible being made between the price of these and genuine soaps. In this country at the present day the household soaps on the market are almost entirely produced by a limited number of manufacturers, each of whom operates on a very large scale and has a reputation which is either already made and thereby traditional, or is in process of acquiring a goodwill equivalent to that established by older competitors. The greater part of the household soap sold is therefore either genuine rosined soap or "run" (e.g. siccated) soap, the latter being retailed at a lower rate; whilst "filled" soaps are disposed of at a still cheaper price. In this way, broadly speaking, the consumer pays according to the market value of the materials present in the soap.

The British export trade in soaps of the household variety is mainly in the cheaper classes, large quantities of "run" and mottled soaps being manufactured for this purpose, together with a greater proportion of "filled" soaps than prevails in the home markets.

Special Classes of Household Soap, such as Carbolic or Naphtha Soaps.—Either "genuine," "run," or "filled" soaps may be crutched with certain organic compounds which find favour with consumers for various uses.

Thus enormous quantities of *carbolic* soap are sold, either the genuine or the run soap base being mixed with a small percentage of phenol, cresylic acid, or tar oil, sufficient to impart the characteristic phenolic odour to the soap. It is the usual custom to tint carbolic household soaps red or reddish-brown. *

Again, incorporation of naphtha or other hydrocarbon oil with soap leads to the production of *naphtha soaps*, for

which a considerable demand also obtains. The presence of the hydrocarbon constituent, as a partial solvent for organic dirt and grease, doubtless assists the detergent power of such soaps, whilst soap solution-hydrocarbon emulsions also aid both detergent value and freedom of lather.

Of late years the substitution for natural hydrocarbons of "hexalin" (hydrogenated phenol or cyclohexanol) and "tetralin" (tetrahydronaphthalene) has been much recommended. These soaps are just as efficient as the older naphtha soaps and are probably gradually superseding the latter.

Naphtha soaps must not be confused with *naphthenic acid soaps*, which (*cf.* p. 182) are the sodium salts of the natural organic acids accompanying certain crude petroleums and are very inferior as regards odour, although of good lathering and cleansing power.

CHAPTER V.—THE PRODUCTION OF DRY SOAPS AND SOAP POWDERS

IN addition to bar soaps, increasingly large quantities of soap are employed in household use in the form of shreds, flakes, or fine powders, the latter being made from soap alone, or, more usually, mixed with soda ash, fine sand, or bleaching agents in order to render them applicable to specific purposes.

It is evident that in washing operations where the articles (*e.g.* clothing or china) are to be cleansed by immersion in a soap solution, it is convenient to have the soap in as readily soluble a form as possible, and that the rate of solution of small fragments of soap will be much greater than that of a tablet or bar. Hence it is not surprising that for such purposes the use of bar soap is being supplanted by that in flake or powder forms.

Dried Soaps in the Form of Shreds or Flakes.—The first section of these soaps to be considered is that of genuine soap. Whilst the fat-charge employed may be somewhat altered from that of a typical bar soap in order to obtain more convenient transformation to the soap fragments, the general procedure is unaltered from that of a genuine soap so far as its manufacture is concerned. A genuine soap containing 63 per cent. of fatty materials is, however, too soft to be shredded into thin flakes or to retain the flakes in a non-cohering state after packing, and therefore the soap is dried, somewhat after the manner of toilet soap stock, until its fatty content reaches 75 per cent. or even higher.

This may be effected in several ways, for example :

(a) Passing the “finished” soap, either in the form of bars or of hot liquid soap, through a continuous drier of the

Procter or Cressoni  type and further dividing the soap shavings, dried to the requisite extent, by means of cutting rolls.

(b) Passing the liquid soap over heated rotating drums, the temperature and speed of rotation being adjusted so that the film of soap on the drum is dried during a passage of about three-quarters of a revolution to the desired degree (about 75 per cent. fatty acids). The dried film is removed by a scraper in the ordinary way, and the thin shreds of soap are in condition to be cut or stamped by machines into smaller fragments of more or less standard and determined size.

(c) Passing the liquid soap into a rapid cooler of the Jacobi or similar type in which it is cast into bars or cylinders of smaller cross-section than usual. The thin bars or cylinders are stacked on trays and dried in a "stove" by a current of heated air until the correct concentration of fatty material is reached, when they are shredded by a mechanically rotating knife.

Whatever the method employed for drying and cutting the soap, the product is intermediate in fatty material or true soap content between a "genuine" 63 per cent. soap and a soap powder (which has to contain still less water in order to crumble down to the powder form). Shredded or flake soaps represent as a general rule, therefore, a very high grade of household soap containing a higher concentration of true soap than the bar variety and very much more suitable for rapid dissolution in water.

Soap Powders.—Certain powdered soaps are also made from genuine soaps by drying the latter on a heated drum, but so as to remove more water than in the case of material which is to be flaked. If the concentration of fatty material is thus raised to about 80 per cent. or even higher, the dried soap is peeled off the drum by the scraper in a condition in which, when cold, it readily crumbles without undue clogging, and it is accordingly comminuted in a disintegrator or mixing mill of one or other of the customary makes.

A particularly neat way of drying and powdering soap is by spraying the soap or soap mixture into a chamber. One

example of this method is the Krause drier. The hot liquid soap (either "genuine" or after crutting with soda-ash or carbonate solution) is forced through a jet in which it comes in contact with an intense and rapidly moving current of hot air. The air disintegrates the thick liquid soap into minute droplets which are carried forward into a "cyclone" separator or large chamber fitted with baffles so arranged that the dried soap is deposited downwards, whilst the air escapes through an upper vent into another subsidiary chamber in which any remaining soap particles are deposited. The drying action of the large volume of air upon the small particles of atomized soap is sufficient to permit, by adjustment of the rate of feed of soap and air, the deposited soap powder to retain only the desired amount of water; whilst the smallness of the particles also causes their rate of cooling to be so rapid that they are deposited at room temperature and show no tendency to clog together.

This machine can obviously be employed either in the manufacture of powdered "genuine" soap or of *washing powders*, i.e. mixtures of soap with fairly considerable proportions of soda ash.

Washing powders, as a rule, are made from hard (*i.e.* tallow or palm oil) soaps, and, in addition to the above method, they are prepared by grinding together the fresh soap base with soda-ash and water, or with crystal soda in a solid mixer, the amount of water being proportioned so as to yield the desired water-content in the final product. In this method a second grinding process in a finer mill or disintegrator is required in order to reduce the first rough powder to one of requisite fineness, the final product being usually mechanically sieved in order to obtain an even grading. They may also be prepared by crutting together the hot liquid soap, soda and water in correct proportions, running the still liquid product into moulds, and breaking up and disintegrating the solid cake produced.

In the manufacture of washing powders it is equally possible to inject molten fatty acids and a strong solution of sodium carbonate through separate jets into a chamber

in which both streams of finely divided mist or spray are thoroughly intermingled. Combination into fine particles of dry soap is thus effected and the product is deposited in the chambers of a separator similar to that described above. This is probably the most economic method of producing soap powders. The original fats are hydrolysed by the modern system of high-pressure splitting followed by distillation of the fatty acids ; the glycerine is thus recovered in a fairly concentrated solution suitable for working up as crude or distilled glycerine (*cf.* Section VII., Chapters I. and II., pp. 424, 436). The distilled fatty acids are then directly combined with sodium carbonate solution in the spray-mixer as mentioned above. This procedure is also the simplest if the soap powder is to be based upon fatty acids derived from the alkali refining or vacuum distillation refining (Section III., Chapter II., pp. 229, 238) of crude fatty oils, or upon "synthetic" fatty acids such as those obtained by the oxidation of hydrocarbon waxes (Section II., Chapter IV., p. 181).

In addition to "genuine" soap powders and washing powders made up of soap and sodium carbonate, there are on the market an ever-increasing number of more or less specialized soap powders designed to serve specific ends.

Thus, for scouring and rough scrubbing purposes, finely ground rock quartz or silica is ground up with dried soap to an intimate, finely divided mixture, which is now most commonly used in the convenient form of a powder, but was formerly made by framing (after crutching) and cutting the cold product into compact cakes or tablets. The abrasive action of the silica serves to loosen films of dirt, or hardened grease, *e.g.* from flooring or pans, and thereby renders them more easily removed by the soap and alkali present.

The incorporation of some dried powdered soap in metal polishing powders is another case of combination of detergents and mild abrasives in the same cleansing material.

Again, for mild blanching of delicate fabrics during washing, it has been found possible to incorporate a small

proportion of a bleaching agent, usually a perborate, with certain "run" soaps containing a good fatty soap blended with sodium silicate. Under suitable conditions of manufacture, the peroxidic compound is blended perfectly evenly with the soap whilst retaining all its peroxide oxygen, and the latter is released when the product is applied in hot solution and serves to brighten articles of apparel without detriment to the colour of the fabric.

Finally, to make the description of washing powders complete, reference may be made to certain solid compounds of sodium carbonate with sodium silicate with which, as a rule, no fatty soap is blended and which are therefore not germane to this volume. Such compounds are, however, similar in type and also in general method of preparation to the saponaceous powders. Of late years, in addition to preparations containing ordinary alkaline or neutral sodium silicate (with respectively 2 and 3·3 mols. SiO_2 per mol. Na_2O), crystalline sodium metasilicate (Na_2SiO_3 , 6 H_2O), sodium hexametaphosphate ("Calgon," $\text{Na}_6\text{P}_6\text{O}_{18}$) and trisodium phosphate (Na_3PO_4 , 12 H_2O) have found similar application. It is not possible in a book of the present kind to deal in more detail with the individual kinds of powdered soaps and derivatives on the market, and it should be noted that, whilst the foregoing description gives a general account of this side of the fat industry, almost every brand of powder has, in its preparation, various factors which determine the exact procedure employed; whilst, needless to say, many of the precise details involved are of the nature of trade secrets and are not disclosed.

CHAPTER VI.—SOFT SOAPS AND TEXTILE SOAPS

Two important classes of soaps remain to be considered, namely, the soft or semi-liquid soaps, and the soaps which are specially made for use in cleansing and scouring fibres in the textile industries. Textile soaps are made both from the soft and the ordinary hard varieties of soap, and the chief sorts are enumerated below after the subject of soft soaps has been discussed.

Soft Soaps.—Much the same range of material is covered by the soft soaps as by ordinary soaps, *i.e.* there are “genuine,” rosined, silicated (carbonated) or “run,” and “filled” (with meal, flour, moss, chalk, etc.) soft soaps; but the demand for soft soaps is not so great as that for the hard varieties and, since the methods of adding the rosin, silicate or carbonate, or solid filling material are practically the same in both cases, it will suffice to describe the production of a high quality soft soap and indicate briefly the characteristics of the lower qualities.

A soft soap of the best quality for household use must be a liquid soap at the ordinary temperature and should be very bright and almost transparent in appearance. This is secured by employing potash, or a great preponderance of potash, as the alkaline base in place of soda, together with a fat-base which will yield as liquid a soap as possible without becoming rancid. The latter conditions, combined with adequate cheapness, are best fulfilled by linseed oil; maize oil and cottonseed oil are also used and also fish oils, menhaden oil, and whale oil, but the high degree of unsaturation of the latter group renders them excessively liable to rancidity. Low-grade olive oil (“sulphur olive oil”) can be used in place of linseed oil, but is more expensive.

Soft soap is prepared both by boiling in the pan and by the cold process.

When made in the pan it is not as a rule grained out with brine, but is finished by evaporation to the correct point. The pan is fitted with closed as well as open steam coils and with a mechanical agitator. The oil charge to be saponified is run in and heated by a vigorous current of open steam, whilst caustic potash solution is added in very slight excess of that necessary for complete saponification and the pan is boiled as in the case of ordinary hard soaps until the process is complete. Then, instead of washing the soap by graining out with brine, open steam is cut off and the excess of water present in the soap is merely evaporated away by heat from the closed coils aided by mechanical stirring to promote the escape of water vapour. Frequently potassium carbonate ("pearl-ash"), or a mixture of pearl- and soda-ash, is added prior to the evaporation, which proceeds until the consistency of the liquid soap, when sampled and cooled on a trowel, reaches a definite stage. At this point the "finished" soap, if made exclusively from potash, contains about 40 per cent. of fatty materials, whilst of course a "finished" soft soda soap will contain at least 60 per cent. of fatty materials.

Soft soaps can also be made by cold process much in the same way as hard soaps (pp. 371-373), and are manufactured to a considerable extent by this method.

By either method the glycerine remains in the soap and cannot be recovered. If it is desired to extract the glycerine from the fats employed, this is effected by hydrolysing them first of all either in autoclaves or by the Twitchell or fermentation processes, after which the fatty acids are boiled in the soap pan with potassium carbonate solution to produce the finished soap. In this way considerable quantities of "distilled oleine," *i.e.* the liquid fatty acids obtained by pressing distilled fatty acids, are worked up into soft soap, chiefly for use in the textile trades.

Finished soft soap is of a semi-liquid viscous nature, but not solid; it is run from the pans or from the cold-process frames into tins, drums, or other containers for sale.

Whilst, as already mentioned, soft soaps are sometimes rosined, "run" with silicate or "filled" with inert solids, probably the most common class of soft soap for household use other than the "genuine" variety is that in which tar oils or hydrocarbons have been crutched in with the soap base in order to increase the emulsifying power and in some cases to confer "disinfectant" properties.

Textile Soaps.—Exceedingly large quantities of soap are employed in the cotton, woollen, and silk industries for scouring and preparing the raw fibres prior to spinning and also for washing the fabrics before or after many of the dyeing operations. Whilst it is not necessary for technical purposes of this kind to prepare the soap in any particular form as regards shape, colour, scent, or wrapping, it is found that the different fibres require definite characteristics in the soap applied in order to give the best results in the finished cloth.

The main requirements for the various kinds of textile goods are as follows :

Cotton Goods.—Raw cotton is not as a rule scoured before weaving, but a grease made from soap similar to good non-rosined household soap and water is used to "soften" the fibres and render them more pliable in the loom. The dyed fabrics are washed after "printing" by the calico printers in order, amongst other things, to remove excess of substances which have been used to "weight" or "stiffen" the material prior to the printing process. Soaps for this purpose must not contain free alkali nor, preferably, should they contain rosin or soaps from seed oils of the maize type ; sulphur olive, Castile, or palm oil soaps, both soft and hard, are the best materials, but soft soap from good quality oleine is also suitable.

For the lower qualities of cottons cheaper kinds of soap are employed, mainly soft or semi-hard soaps from oleines with some linseed oil soaps.

Woollen Goods.—The raw wool requires scouring with soap solution in order to reduce the wool grease present to the desired proportion. The waste liquors from the scouring

process are too objectionable and too large in quantity to be run directly into streams as works effluent, and they have therefore to be boiled with mineral acid in order to liberate the wool grease, which is collected and forms a more or less waste product, except for the production of lanolin from the highest grades, as described in Section II., Chapter II. (p. 138). It has been proposed to extract the grease from the raw wool by various solvents, but those tried up to the present have also exerted a detrimental action on the wool itself, although it has been suggested that controlled extraction by acetone avoids this difficulty and also gives a wool fat of relatively high quality.

The soap-scouring process, however, at present holds the field, the best soaps for the purpose being free from caustic alkali (although a certain proportion of carbonate or silicate is not inadvisable); soft soap made from potash and linseed oil is suitable, whilst soft ammonia soaps are still better. Soft soaps from oleines are also very widely used for high-class work, having less tendency to "gumminess" than the linseed oil soaps.

After the wool has been spun into yarn it is again scoured, and at this stage Castile or mottled soaps are often used, although linseed oil soft soap is also employed by some. It appears, however, to be advantageous in this operation to employ a soap of medium hardness, sulphur olive or Castile soda soaps probably representing the best all-round quality.

After the yarn has been dyed, it is again washed and also after the final weaving into cloth. In both cases, for high-class goods, the scouring should be carried out with alkali-free soft (usually potash) soaps made from sulphur olive oil or from a good tallow and nut oil base, the tallow predominating.

Except for scouring the spun yarn (and here only to a slight extent) and for scouring "shoddy" (*i.e.* recovered wool from old cloth, etc.), the presence of free alkali is inadmissible; for "shoddy" the use of alkaline soaps is preferred, possibly because the woven fibres of the old

fabric are broken down more readily owing to the hydrolytic action of the free alkali present.

Silk Goods.—The raw silk is washed with soap solution in order to loosen or “degrain” the fibres, and here again a strictly neutral soap is required. For the best silk a pure olive oil soap may be used with advantage, good quality Castile or palm oil soap being an admissible substitute.

The spun silk goods are washed with soda or potash soaps made from sulphur olive oil or distilled oleine of good quality.

Other Industrial Soaps.—The above list does not embrace by any means the whole of the special soaps which are used for one or other purpose in the textile and allied industries, but will give some idea of the general properties which are needed. The main feature of most of the soaps described is absence of free alkali (save in exceptional cases) combined with the presence of a more or less pure fatty soap of a readily soluble and free-lathering nature—hence the abundant use of the soft soaps.

Similar soaps to those used for washing dyed fabrics are also largely employed in processes ancillary to the bleaching of cotton and woollen goods, whilst in certain cases dealt with in the next chapter the soap or fatty acid enters into the actual process of dyeing and is therefore something more than merely detergent in its action.

Reference may also be made here to a certain amount of soap-scouring which is carried on in connection with animal hides, for which soft soaps made from relatively low-grade oils are quite suitable, providing they do not contain more than a little free alkali: further consideration is given to these in the chapter dealing with the use of fatty materials in leather-dressing (pp. 509–511).

In addition to soaps, a number of the “soapless detergents” which are briefly discussed in the next chapter find increasing use in the textile industries, either for washing or scouring, or as wetting, dispersing, or stripping agents.

CHAPTER VII.—“SULPHONATED OILS” (“TURKEY RED OIL”), ALKYL SULPHATES OR SULPHONATES, AND OTHER FATTY DERIVATIVES NOW EMPLOYED AS “SOAPLESS DETERGENTS”

ALTHOUGH many semi-synthetic fatty compounds (comprising sulpho- and/or amino-derivatives) have been evolved in recent years as wetting-out, emulsifying, dispersing or detergent agents of marked activity, the employment of this class of substances originated about seventy or eighty years ago, when it was found that unsaturated oils, either of the olive or fish oil types, or more especially castor oil, interacted with sulphuric acid to form so-called “sulphonated” oils. These “sulphonated” oils furnish alkali salts, the aqueous solutions of which have the property of holding in solution considerable proportions of either fatty or hydrocarbon oils. “Sulphonated” castor oil came to be known as “Turkey red oil” because the mixture of alkali salt of the product together with unaltered castor oil was found to be a particularly useful assistant in cotton dyeing and printing with alizarin dyestuffs such as Turkey red. It acted very similarly to a mordant, at the same time brightening and adding lustre to the dyed fabric. The cotton goods were dipped in an emulsion of water containing about 5–6 per cent. of Turkey red oil, and subsequently steeped in the dye-bath and finished in the usual manner. The utility of the Turkey red oil is now considered to be as much due to its wetting and emulsifying powers as to any actual mordant action; for it has frequently proved equally useful with dyestuffs which do not require a mordant.

Similar “sulphonated” products from non-hydroxylic fatty oils had also been produced by treating distilled oleines, olive oil, fish oils, sperm oil, etc., with sulphuric acid and converting the products into alkali salts. These found,

and still find, their chief uses as filling materials for leather prior to tanning, as ingredients of special lubricating oils (notably "cutting oils" for machine tools), and also in the manufacture of a special class of soaps (Monopol or Tetrapol soaps) made by saponifying greases, bone fats, or tallows in presence of from about half to an equal proportion of a "sulphonated" oil. Such soaps may be as hard as a good tallow soap, yet lather as freely as a nut oil soap in consequence of the presence of the "sulphonic" derivatives; moreover, they will retain in the emulsified state a considerable proportion of added components, such as mineral oil, chlorinated hydrocarbons, or hexalin (hydrogenated phenol), etc. These products find considerable use on the Continent, and to some extent in England, in the scouring of some classes of textile fabrics.

More recently it was realized that the maximum development of specific properties such as wetting capacity, emulsive and dispersive power, or detergency was associated with the presence of an alkyl chain of varying length (but from about C₁₂ upwards) and also of a terminal, strongly polar group (whether anionic or cationic, most usually the former). This has led to the production, or to patents being taken out for the production, of a very large number of individual compounds of various types; these as a group are often referred to at present as "soapless detergents" or "textile assistants," to distinguish them from the ordinary soaps (alkali salts of higher fatty acids). It is impossible here to give an adequate account of all the compounds which have been proposed or put on the market since about 1930, and discussion will be confined to a comparatively small selection from the following classes:

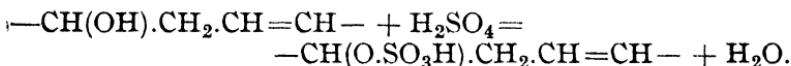
1. The older "sulphonated" oils.
2. Salts of the monosulphuric esters of higher fatty alcohols, or of higher alkyl sulphonates.
3. Higher acyl derivatives of hydroxy- or amino-alkyl-sulphonic acids (Igepons).
4. Alkylated aromatic sulphonic acids.
5. Triethanolamine salts of higher fatty acids.

6. Quarternary ammonium compounds containing a long-chain alkyl group.

7. Fatty acid esters of polyglycerols.

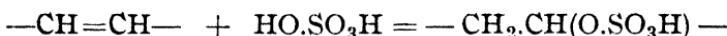
1. "**Sulphonated Oils.**"—In these compounds the strongly polar sulpho-group appears in the centre or thereabouts of a C₁₈ alkyl chain and the specific properties of the products, although useful, are not so highly developed as in compounds in which the polar group terminates a long alkyl or acyl carbon chain. Hence for many purposes the "sulphonated oils" are being replaced by one or other of the more recent preparations.

The action of sulphuric acid on the fatty oils is twofold. In the case of castor oil, it is mainly one of esterification of the alcoholic hydroxyl group present in ricinoleic acid :



The characteristic emulsifying and other properties of Turkey red oil are mainly conditioned by those of the corresponding sodium salt : (---CH(O.SO₃Na).CH₂.CH=CH---).

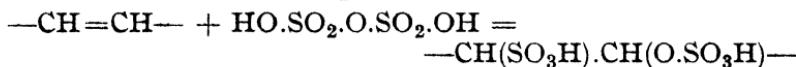
In the addition of sulphuric acid to the ethylenic bonds of an unsaturated acid or oil, on the other hand, it is now generally agreed that the product is also a monosulphuric acid ester, formed by addition at the double bond thus :



The oils have, therefore, not been sulphonated, but "sulphated," and the term "sulphonated oil" does not convey an accurate picture of the process. Other side reactions proceed concurrently during either of the above two main actions. The sulphate group is fairly easily removed in an acid medium in presence of moisture and consequently the final product contains a certain proportion of hydroxy-acids. Further, estolides and possibly other anhydride-like compounds are produced during the reaction by elimination of water between the alcoholic hydroxyl group of one molecule of sulphated fatty acid and the carboxyl (or possibly acid sulphate) groups of another. Finally, in the case of sulphate

tion of oils, the sulphated derivatives have the typical constitution of fat-splitting (hydrolytic) agents, and considerable production of free fatty acid, sulphated or otherwise, from neutral oil, usually takes place during their manufacture.

On the other hand, production of true sulphonic derivatives, in place of or accompanying the "sulphated" products, may occur if the action is allowed to take place under strongly dehydrating conditions and, especially, if fuming sulphuric acid (oleum), sulphur trioxide, or chlorsulphonic acid is used in place of sulphuric acid as the "sulphonating" agent. In these cases the action probably takes a course such as :



The acid sulphate group in the complex formed is comparatively easily hydrolysed during subsequent washing of the product with water, and true (hydroxy)-sulphonic acids, $\text{—CH}(\text{SO}_3\text{H})\text{.CH(OH)}$, and their condensation products, are present in the material finally obtained. These compounds will, of course, be completely stable in so far as the direct attachment of the sulphonic group, $-\text{SO}_3\text{H}$, to a carbon atom is concerned, whereas the hydrogen sulphate groups of Turkey red and the ordinary "sulphonated" oils and oleines are liable to hydrolyse in presence of water or dilute acid, yielding free sulphuric acid and a neutral hydroxy-fatty compound ; as between the true fatty (hydroxy) sulphonates and the unhydrolysed sulphate derivatives of the type of Turkey red oil, there is probably little to choose on the score of relative efficiency. Claims that the true sulphonates are more effective textile assistants may in reality be based upon their greater stability, which is due to their incapacity to lose the polar sulpho-acid group by hydrolytic action.

Technical Production of "Sulphonated" (Sulphated) Oils.
—The oil is well agitated in a lead-lined vessel fitted with cooling coils through which cold water can be run. About 25-50 per cent. of its weight of cold concentrated sulphuric acid is slowly run in, the rate of addition being controlled

so that the temperature is maintained below a certain limit, which is determined by the point at which more profound changes set in, wherein the sulphuric acid is reduced and sulphur dioxide commences to be formed. In the case of Turkey red oil from castor oil, the temperature may be allowed to approach, but not to exceed, 35° C. ; with oleines or rape oil a somewhat lower limit is safer, and the less saturated oils (*e.g.* linseed or whale oil) are better treated at or below 10° C., in order to minimize the tendency for undesired side reactions to develop.

After all the acid has been added, agitation and cooling are continued for some little time, and then sufficient water is added to remove the greater part of the uncombined sulphuric acid. The aqueous acid layer is settled and drawn off, and the "sulphonated" oil is washed free from mineral acid with sodium sulphate solution and finally partially neutralized with soda (or, better, with ammonia) until a point is reached at which the product is completely miscible with cold water.

The oil is then ready for use in the dyeing industry, whilst it is also suitable for conversion into textile soaps.

As previously mentioned, a mixture of low-grade greases or tallow and the "sulphonated" oils yields on complete saponification a soap which is sufficiently hard and detergent to replace the ordinary household type in many technical scouring operations. It should be pointed out that the soaps from "sulphonated" oils cannot readily be salted out, and that in consequence this type of soap must be manufactured by a similar procedure to that used for soft soaps (p. 392). The "sulphonated oil" soaps also possess the property of holding much larger amounts of filling materials (including especially hydrocarbon oils and related derivatives such as tetralin or hexalin) than the ordinary genuine soaps, and considerable quantities of "sulphonated oils" are used on the Continent in the production of naphtha soaps of various kinds.

For Turkey red oil, castor oil is the best raw material, but non-drying or semi-drying oils of the olive, rape, ground-

nut or cottonseed type have also been employed, whilst partially hydrogenated whale or fish oils are also serviceable for the purpose.

Characteristics and Analysis of "Sulphonated" (Sulphated) Oils.—As already indicated, more than mere formation of a sulphated derivative of a fat or fatty acid takes place during the process of manufacture of these oils; some of the sulphate groups are hydrolysed to the corresponding hydroxy-derivatives, and various condensations (estolide or semi-anhydride formation) may subsequently occur. Consequently, unless the raw material and the conditions of treatment with sulphuric acid, and subsequently water and mineral salt solutions, are all constant within narrow limits the composition of the products is liable to vary. Furthermore, the amount of combined sulphuric acid (as $-\text{CH}_2\text{O}\text{SO}_3\text{Na}$) in the products never approaches that required by complete conversion of all hydroxy- (castor oil) or ethenoid- (oleines, olive oil, etc.) groups into the corresponding sulphated derivatives. The technical analysis of these products has therefore developed on the usual semi-empirical lines, for a discussion of which the reader is referred to other monographs (*cf.* References to this Section, p. 408). The chief characteristics usually determined include the amount of unattacked neutral fat (often mis-termed the "unsaponifiable" or "unsaponified" fraction), the total ash content (a measure of the total sulphur as sodium sulphate), the sulphur combined with the fat as sulphate ester (also as sodium sulphate, from which the amount of admixed sodium sulphate in the product can also be determined), the iodine value and sometimes also the hydroxyl or acetyl value of the material.

2. Salts of the Monosulphuric Esters of Higher Fatty Alcohols, or of Higher Alkyl Sulphonates.—The higher fatty alcohols can now be technically manufactured by catalytic hydrogenation at high pressure and temperature of the corresponding fatty acids or esters, as described in Section III. (Chapter III., p. 264). Reduction of fatty oils by this means gives a mixture of alcohols corre-

sponding with the component fatty acids in the original fat treated, and these may be separated partially or completely, if desired, by fractional distillation under reduced pressure.

The sodium salts of the hydrogen sulphates of these alcohols, $R.CH_2.O.SO_3Na$, especially those of dodecyl (lauryl), hexadecyl (cetyl) and oleyl alcohols, have found useful applications as detergents and wetting-out agents. The calcium and magnesium salts of these monosulphuric esters are soluble in cold water, so that the sodium salts can be used as effectively in hard as in soft water. As strong electrolytes, these salts are little affected by dilute mineral acids and can therefore also be used as detergents in dilute acid media, subject to some minor hydrolysis (marked in hot solutions) of the sulphate ester group, with regeneration of the higher fatty alcohols. It is possible to convert the higher alcohols into their hydrogen sulphates by warming with concentrated sulphuric acid, but in technical practice it is preferred to treat the alcohols in hot pyridine solution with sodium pyrosulphate, or alternatively with sulphur trioxide. The technical sodium salts are recovered by diluting the reaction mixture with water, exactly neutralizing with caustic soda solution, and salting out with brine or sodium sulphate solution.

(The corresponding sodium salts of phosphoric acid esters of the higher alcohols may be obtained by similar means.)

The corresponding true sulphonnic acids, $R.CH_2.SO_3H$, are more difficult to prepare, but their alkali salts have similar detergent and wetting properties to those of the class just discussed, and are stable not only to hard water but also to dilute mineral acids. Indeed Reychler, who was the first to study the properties of cetyl sulphonnic acid in detail, noted the detergent properties of the free acid, which he termed a "hydrogen soap." Their relative inaccessibility alone prevents them from finding technical applications on the same scale as the sodium sulphates of the higher alcohols.

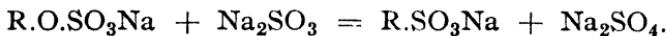
They can be prepared by oxidation of the corresponding mercaptans or disulphides with nitric acids :

$R.OH \rightarrow R.Br \rightarrow R.SH$ (or $R.S.S.R$) $\rightarrow R.SO_3H$,
whilst their sodium salts result directly when the higher

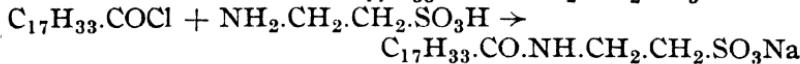
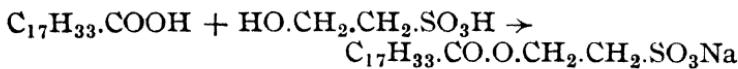
alkyl halides are heated under pressure with aqueous sodium sulphite :



or when the corresponding sodium alkyl sulphates are similarly heated with aqueous sodium sulphite :

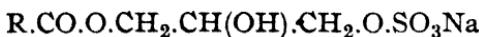


3. Higher Acyl Derivatives of Hydroxy- or Amino-alkylsulphonic Acids.—Condensation products of oleic acid with β -hydroxy- or β -amino-ethylsulphonic acid yield sodium salts with pronounced detergent activity and good stability to dilute aqueous solutions containing calcium or magnesium salts or mineral acids. They are prepared by heating oleic acid or its chloride with either isethionic acid (β -hydroxyethylsulphonic acid) or taurine (β -aminoethylsulphonic acid) and converting the products into sodium salts :

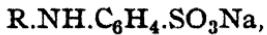


The oxy-condensation product is very similar to sodium oleyl sulphate in its detergent power and in the stability of its solutions ; it is not completely stable to dilute mineral acid, whereas the amino-condensation product is entirely unaffected by aqueous mineral acids and hard water, and possesses excellent detergent properties.

A large number of similar synthetic compounds in which a higher acyl or higher alkyl group is joined through oxygen or the amino-linking to a polar group terminating in $-SO_3Na$ or $-O.SO_3Na$ has been prepared and claimed in various patents. As illustrations, compounds in the acyl series represented by such structures as



may be instanced or, in the alkyl series,



So far as is known, however, the above oleic derivatives of hydroxy-and amino-ethyl sodium sulphonates (and possibly the corresponding sodium sulphates) are the most widely applied technical forms of this group of compounds.

4. Alkylated Aromatic Sulphonic Acids.—Certain substituted naphthalene sulphonic acids which have found use as fat-splitting agents (Section III., Chapter IV., p. 275) give alkali salts with valuable emulsifying, wetting, etc., properties. Of these, the sodium salts of isopropynaphthalene sulphonic acid and some of the butylnaphthalene sulphonic acids may be mentioned.

5. Triethanolamine Salts of Higher Fatty Acids.—The compounds discussed above (classes 1 to 4) all share in common the presence or introduction of a sulphate or sulphonic grouping as the salt-forming part of the active detergent, wetting, etc., agents. We pass, in the present class and the next, to other compounds in which the salt-forming parts of the "soapless detergents" are nitrogenous (amino) and not sulpho-acid groups. (This broad classification does not preclude the presence of subsidiary amino- or imino-groupings in the sulpho-acid class)



or of subsidiary sulpho-groups (e.g. metho-sulphates) in some of the amino-derivatives covered in class 6.)

From another standpoint, it should be pointed out that the nitrogen-containing "soapless detergents" may possess the active long-chain acyl part of the molecule in either the anionic or the cationic part of the molecule. The present class (5) represented by triethanolamine salts of the higher fatty acids, falls into the same category as the sulpho-acid compounds of classes 1-4 and the ordinary soaps in that the active part of the molecule is still the anion of the compound when dissociated in aqueous solution.

Ethylene chlorhydrin, $Cl.CH_2.CH_2.OH$, interacts with ammonia to give, successively, β -aminoethyl alcohol, $NH_2.CH_2.CH_2.OH$, diethanolamine, $NH.(CH_2.CH_2.OH)_2$, and finally triethanolamine, $N(CH_2.CH_2.OH)_3$. The soaps

of the ordinary higher fatty acids with the latter hydroxylated tertiary base have more pronounced wetting and also emulsifying powers than the sodium or potassium soaps, and the triethanolamine soaps have found considerable use as ingredients of shaving creams (applied without a brush, *cf.* p. 377) and as emulsifying agents for castor, almond or olive oils when the latter are components of "oil shampoos" for the hair. They are stated to lubricate as well as assist in cleansing the hair, and to avoid excessive removal of hair fat and consequent "drying" of the scalp.

6. Quaternary Ammonium Compounds containing a Long-chain Alkyl Group.—We come next to the amino-class of textile assistants in which the active part resides in the cationic part of the salt molecule; here the long-chain alkyl groups are components of secondary or, more usually, tertiary amines. The cation-active compounds are not usually good detergents, but may have marked wetting or dispersive powers in suitable cases.

The most usual forms of compounds proposed in this class are halides of quaternary ammonium bases in which one radical is a long-chain group such as cetyl, $C_{16}H_{33}-$, or oleyl, $C_{18}H_{35}-$. Important examples include cetyltriethylammonium iodide, $C_{16}H_{33}.N.(C_2H_5)_3I$, cetyl-diethylammonium halides (X), $C_{16}H_{33}.N.(C_2H_5)_2HX$, or cetylpyridinium bromide, $C_5H_5.N(C_{16}H_{33})_3Br$, but many others of similar general structure have been patented.

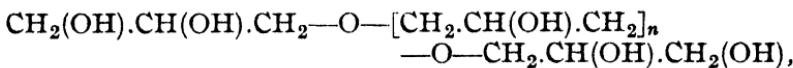
Another group of cation-active compounds, termed sapamines, are derived from ethylene diamine and consist of monoacylated ethylene diamine with the second amino group converted into a quaternary ammonium salt; for instance, derivatives of oleic acid such as



The quaternary ammonium group may contain ethyl, phenyl or benzyl in place of methyl, and halides may be employed in place of the methosulphate shown in the formula.

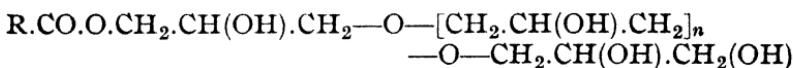
7. Fatty Acid Esters of Polyglycerols.—It was mentioned in connection with edible fats (Section IV.,

Chapter II., p. 302) that monoglycerides, for example, mono-palmitin or mono-olein, are useful emulsifying agents in margarine or cooking fats. The simple monoglycerides are, of course, practically insoluble in water and do not belong to the class of "soapless detergents." On the other hand, when glycerol is heated in presence of suitable catalysts, condensation products of the type of ethers are produced by union of two or more (usually four or five) molecules of the polyhydric alcohol. These are known as polyglycerols, their general formula being



where n may be 0, 1, 2 or 3.

If tri-, tetra-, or penta-glycerol is esterified with a higher fatty (e.g. oleic) acid so that not much more than one equivalent of the acid is in combination with the poly-glycerol, the resulting product, of the general formula

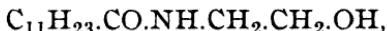


is a neutral or non-dissociable compound which (owing to the high proportion of glycerol-like hydroxyl groups present) is freely soluble in water and on which the long-chain acyl group confers the typical properties of a soap. This class of compounds therefore represents a case in which a non-ionizable substance can replace detergents or surface agents which depend for their activity on specific anionic or cationic groups. Such compounds are of course unaffected by hard water, since they do not form salts with metallic bases, and also by aqueous solutions of mineral acids, although they are naturally hydrolysed to fatty acid soaps and free polyglycerols by aqueous solutions of caustic alkali.

The above *classification of the newer semi-synthetic textile assistants* is only superficial, since it is impossible completely to differentiate the numerous types, which frequently overlap. It was noted (p. 404) that division according to the nature of the polar group employed (sulpho-acid or nitrogen base) is partly obscured by the fact that sulphonic or

sulphate derivatives of amido-compounds on the one hand, and methosulphates or other sulpho-derivatives of amino- or quaternary ammonium compounds on the other hand, have frequently been suggested as useful members of the group.

To illustrate further the possible extent of overlapping of this kind, the case of acyl derivatives of β -aminoethyl alcohol may be cited. β -Dodecylamidoethanol,



is a compound with definite wetting-out properties but not high solubility in water. Conversion of the alcoholic group to the sodium salt of its monosulphuric ester,



gives a product of much greater solubility and higher detergent and wetting-out powers ; this derivative now belongs to class 3 (above) whereas the original substance belongs rather to classes 5 or 6. Again, if, instead of sulphation, it is condensed with ethylene oxide, the product so obtained, $\text{C}_{11}\text{H}_{23}.\text{CO.NH.CH}_2.\text{CH}_2.\text{O.CH}_2.\text{CH}_2.\text{OH}$, like those of class 7, is a neutral water-soluble compound with comparatively efficient wetting-out and detergent properties.

It has already been pointed out that the number of specific variants of the different types of "soapless detergents" which have been proposed or patented is enormous, and the foregoing summary is only intended as a general guide to and survey of this field.

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SECTION VI.—THE USE OF FATS IN CANDLES AND ILLUMINANTS

Introductory.—Fats and waxes are employed as illuminants either in the form of lamp oils or in candles. The use of fatty oils in lamps was formerly very extensive, but of course, in Western Europe, America, and other parts of the world petroleum oils have now very largely displaced liquid fats for this purpose. There still remain, however, extensive regions, including, for example, parts of Russia and Scandinavia, India, or China, in which fatty oils are employed for burning in lamps.

In the candle industry the development of modern methods of lighting has had a somewhat different effect, for, in spite of the abundant gas and electricity facilities, the candle trade has continued to grow. At the same time, the amount of fat employed by the trade has remained more or less stationary for many years, because the main constituent of the present-day candle is solid paraffin produced from the fractionation of crude mineral oil. Doubtless the advent of large supplies of paraffin wax, as a result of the development of the petroleum industry, would have led to the elimination of fatty compounds from candles except for two factors :

(i) The price of high-grade paraffin wax approximates to that of tallow and is higher than that of pale "stearine" produced by expression of the fatty acids distilled from hydrolysed greases and other fats of a low grade.

(ii) Paraffin candles *per se* have a tendency to bend out of shape at the ordinary temperature and lack the rigidity of a stearine candle. On the other hand, they are clearer

and brighter in appearance and burn somewhat better than a pure tallow candle, and it has been found that a candle composed of about 97 per cent. of paraffin wax and 3 per cent. of "stearine" (*i.e.* tallow fatty acids) gives the best all-round product as regards rigidity, colour, and burning properties; these proportions are variable within certain limits.

Probably about 3,000 tons of fatty acids are used every year in Britain in the production of candles of this type, whilst the United States, Germany, and France consume amounts of about the same order of magnitude in candle manufacture.

In the present section of this book a brief description is given of the means of production of the fatty material used in candle manufacture, with some account of the actual manufacture of candles; in a further chapter the chief fatty oils which have been, and in some cases still are, employed in lamps of various types are reviewed.

CHAPTER I.—THE MANUFACTURE OF CANDLES FROM FATTY MATERIAL

CANDLE material is made in three main varieties : (i) dips and tapers, (ii) candles, and (iii) night-lights.

In each case the preparation of the wick is an important feature. The modern wick consists of cotton strands of good quality woven into a thin plait ; the plaited structure causes the wick, when burning, to bend over so that its tip projects through the non-luminous part of the flame to the outside, where there is a sufficient supply of air to burn it more or less completely away. By this means the old-fashioned "snuffing" procedure is almost completely eliminated. The freshly plaited wicks are steeped or "pickled" in a solution of an inorganic salt or salts such as borax or nitre, the principal object being to adjust the rate of combustion of the wick as nearly as possible to that of the candle material itself ; after pickling, the wick material is centrifuged and then dried in hot air before being wound on spools ready for use in the candle machines.

Dips and tapers are made by simply suspending a number of lengths of wick from a rack or "wheel" in a tank of melted stearine or paraffin wax, or a mixture of both, and withdrawing the whole from the liquid. After solidifying they may be re-dipped in order to increase the thickness of the fat and wax layer.

They are also prepared by continuous winding of a length of wick from a spool through a pan containing melted stearine or paraffin wax, then through a die of definite diameter (from $\frac{1}{16}$ inch upwards) and on to a second drum. The process is repeated a second or third time in order to obtain a taper about $\frac{1}{8}$ inch in diameter, the final drum being

unwound and the finished material cut into lengths before it has set completely hard.

By repetition of this process until the candle is $\frac{1}{4}$ inch or $\frac{3}{8}$ inch thick, the small paraffin candles frequently employed for decorative purposes are produced, but the dipping process is not now used for candles of greater diameter than these.

Candles.—It has already been stated that the modern candle is made almost always from a mixture of paraffin wax with a minor proportion of higher-melting fatty acids or "stearine."

The preparation of the "stearine" is the only part of the operation which involves the technology of the fatty oils. The fats employed are usually tallows and palm oils of fair quality, but stearines derived from the hydrolysis of greases and low-grade fats are also used. Many attempts, not invariably successful, have been made to employ hydrogenated fats of various kinds as candle material. The physical state in which the solid fatty acids are deposited from the liquid phase is the important factor in suitability for use in candle manufacture, the ideal condition being one in which small crystals are produced in a close, firm texture. This state is well represented by the palmitic-stearic acid eutectic complex, whereas if either individual acid predominates largely the crystal structure is built up of relatively large waxy laminæ in which the combination of flexibility and rigidity, which is necessary in a candle, is not to be found. Consequently hydrogenated oils of the linseed, sunflower seed, or soya bean type, which contain over 90 per cent. of acids derived from stearic acid, or of the whale or fish oil type, in which stearic, arachidic, and behenic acids will predominate, are not to be expected to yield such good results as tallow fatty acids; the acids from hydrogenated palm oil might be more serviceable in this respect.

Preparation of "Stearine" for Candle Material from the Fats.—The candle worker is not concerned to obtain the fatty acids as soaps; indeed the manipulation of

soap is an unnecessary complication from his point of view. At the same time he will desire to recover the glycerine present, so long as market prices of the latter are attractive, and therefore the method usually adopted is a combination of the fat-splitting and sulphuric acid saponification processes discussed in Section III., Chapter IV. (pp. 271, 279).

In order to recover the glycerine present in the neutral fats, the latter are usually first of all hydrolysed by the autoclave process (*cf.* p. 271), although the Twitchell process is also used, but not so much in this country as on the Continent and especially in America.

The autoclaved fatty acids should not contain more than 2 per cent. of neutral fat, and may be used at once for expression and recovery of the "stearine" or candle material if their colour is sufficiently bright. In the majority of cases, however, it is preferred to distil the acids prior to pressing in order to obtain a perfectly pale-coloured "stearine."

At this stage, therefore, the autoclaved acids may be submitted to a "sulphuric acid saponification" (*cf.* p. 279) and also distilled. The older process of distillation at atmospheric pressure in a current of steam superheated to about 300° may be used, or the newer method of distillation without steam in a vacuum may be adopted. The quality and the yield of distilled acids by the older process have been much improved by constructing the distillation plant, and especially the condensing systems, in acid-resisting steels or similar alloys. The use of resistant metal, together with improvements in the gas-firing of the distilling pots, results in the production of comparatively pale-coloured fatty acids. On the other hand, for distillation of straight "oleines" which have not been submitted to the sulphuric acid treatment (and for which the presence of steam is therefore not required in the transformation of sulphato- to hydroxy-stearic acids) the vacuum process is very satisfactory. It operates at about 200-220° with a vacuum of about 5 mm. of mercury; heat can be supplied through closed coils by circulating heated oil or suitable specific organic compounds (*e.g.* diphenyl), the vacuum still can be

made to operate continuously and to yield very pale, almost colourless, fatty acids.

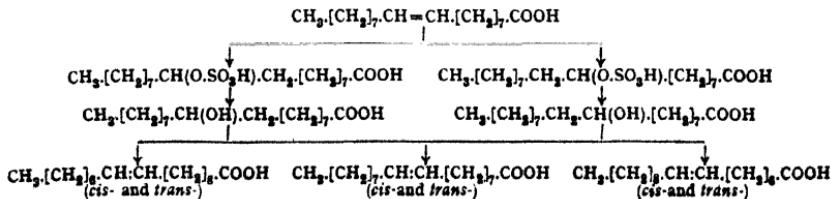
The combination of both means of hydrolysis is termed the "mixed saponification process," and has the following advantages :

- (i) As much glycerine as possible is recovered for concentration and distillation (*cf.* Section VII., pp. 424, 428).
- (ii) Complete hydrolysis of all neutral fat is effected.
- (iii) The quality of the "stearine" finally produced is better when the fatty acids have been distilled.
- (iv) The yield of "stearine" from the original fat, which is not more than 50 per cent. in the absence of distillation, reaches somewhat over 60 per cent. when the distillation process is applied.

The increase in the yield of solid material is due to the partial conversion of liquid oleic acid, under the influence first of sulphuric acid and then of steam, into solid derivatives : the sulphuric acid reacts additively with the ethylenic linkage and produces sulphated stearic acids (Section V., Chapter VII., p. 398), which in presence of steam at a high temperature revert to sulphuric acid and simple mono-hydroxy-derivatives with the following ultimate results :

(i) Solid hydroxystearic acids are formed to varying extents.

(ii) Elimination of water from each of the hydroxystearic acids takes place in either of two possible ways, and this gives a final mixture of isomeric oleic (octadecenoic) acids which contains, in addition to ordinary oleic acid, elaidic acid, and also (to a smaller extent) both the *cis*- and *trans*- forms of $\Delta^{8:9}$ and $\Delta^{10:11}$ oleic acids. The mixture of solid isomerides of oleic acids so produced melts at about 45°.



The proportion of solid ("iso-") to liquid oleic acids in the distilled acids has been shown to be approximately 66 per cent. to 34 per cent. (*i.e.* the equilibrium ratio of elaidic to oleic forms, *cf.* Section I., Chapter II., p. 14). The presence of hydroxystearic acids and of these *iso*-oleic acids modifies the crystal structure of the palmitic-stearic acid mixture present in the expressed "stearine" which is employed in candle manufacture, and confers a toughness and appearance which causes this product to be preferred for candles made entirely from stearine (without paraffin wax). For ordinary paraffin candles, the 3 per cent. or thereabouts of "stearine" which is added is, however, preferably made without sulphuric acid saponification and consists of a simple mixture of, usually, about 70 per cent. of palmitic with 30 per cent. of stearic acid.

The fatty acids ultimately obtained, whichever of these modes of procedure has been followed, are in the state of somewhat yellow or amber coloured liquids which on cooling deposit a large amount of crystalline solid fatty acids or "stearine," which must then be separated from the liquid "oleine" present.

Separation of the Distilled Fatty Acids into "Stearine" and "Oleine."—The distilled fatty acids are first of all cooled artificially to promote crystallization and then pressed by hydraulic power in an apparatus of somewhat similar construction to an ordinary filter-press. The cooling process requires considerable adjustment: if the rate of cooling is too rapid the solid acids separate in very small crystals or in the form of an amorphous "mush" which holds the liquid acids tenaciously, whilst, as already indicated, the separation of crystals of too large a size (too slow cooling) leads to an inferior texture of the press-cakes and also causes difficulty at this stage in pressing out all the liquid from between the large laminated crystals.

The distilled acids are therefore placed in shallow aluminium, tin, or other acid-resistant trays which are stacked in a cooling chamber the temperature of which is regulated by refrigeration. The temperature is gradually

lowered, so that crystallization sets in evenly and in the desired state of aggregation, and is maintained at about 10° C. for several hours.

The contents of the trays are packed into the "cold press" and submitted to hydraulic pressure in order to remove the greater part of the liquid acids. These go to form the "oleine" or commercial oleic acid of trade, after a further refrigeration in tanks in the course of which more solid acid is usually deposited and recovered by fresh pressing.

The cold press-cake is then remelted and again submitted to the above described process at a higher temperature. The hot press is similar in construction to the first-named, except that each section is divided by a double-walled steel compartment into which steam can be admitted. The temperature may be maintained at about 35° C., in order to obtain "stearine" of the desired melting point. It is then almost white in colour, and may be further bleached by exposure to air and sunlight. The liquid acid drainings from the hot pressing set again on chilling to a mass of similar consistency to the original cooled distilled acids and are re-worked with the latter.

Moulding of Candles from Stearine and/or Paraffin Wax.—The moulding of candles is effected in moulding machines which consist essentially of a nest of pewter tubes secured at the top and bottom to tube plates and encased in a box through which water can be made to circulate round the outside of the tubes. The wick is supplied from separate spools to each mould, passing through the hollow piston which is used to eject the finished candle. When first starting, the wick is drawn up through the mould and secured by some means to the top.

The mixture of paraffin and stearine is melted in tanks (a little oxalic acid being added if necessary in order to precipitate any traces of calcium salts present); the clear liquid is then poured into the moulds and allowed to cool. The short "dummy candles" so produced are then ejected by raising the plate on which all the pistons are mounted and forcing the dummies into a wooden or metal clamp

placed over the moulds. They are secured in this clamp and thus hold the wick centrally in the moulds.

A fresh supply of melted material is then run into the moulds while the wicks are thus supported and cold water is run into the tank surrounding the moulds. So soon as the candles are set, they are pressed upwards by the vertical pistons, secured in the upper frame or clamp, the wicks cut by means of a sharp knife, the clamp removed, and the candles stored in trays. The excess wax on top of the moulds is then scraped off with a sharp knife, the clamps replaced, and the operations gone over again.

For producing candles with self-fitting ends to fit the holder or sconce, the upper portion of the mould is split down the centre and tightly clamped together, then the liquid wax is poured in. When the candles have set, this upper portion can be opened out (by a lever which operates all the butt-moulds in the frame at one movement), so that the tapering butt end of the candle has a free passage when the piston is moved upwards.

Paraffin candles are cast from wax at a temperature of about 50° C., stearine candles at about 80° C., and the usual mixed variety at about 60° C.

In the manufacture of tinted candles the colour is introduced, in the form of aniline dyes, in solution in the "stearine" before adding this to the paraffin when preparing the melted mixture. The various ornamental varieties of fluted or spiral candles, etc., are produced either by special forms of moulds or by subsequent turning in a lathe, and depend upon mechanical devices which need not be discussed in detail here.

Beeswax and Spermaceti Candles.—Many years ago, before the era of stearine, much less of paraffin candles, these articles were made from beeswax or spermaceti for the use of the wealthier classes, whilst others had to be content with tallow "dips." The use of beeswax and spermaceti has persisted in a minor degree, and candles are still made of these materials for ceremonial use and for special purposes.

Beeswax candles cannot be moulded in the same manner as the modern candles to yield a product of the correct appearance and they are prepared, largely by hand, by what is known as the pouring method. This is a variant of the dipping process in which the melted beeswax is poured over the wicks, the latter being strung from a frame which is rotated. With alternate cooling in air after successive pourings, the procedure is repeated until the candles are of the requisite thickness, when they are cooled and placed on a marble slab and rolled by manual pressure with a flat board until a perfectly rounded shape is attained.

The extent of the trade in this expensive class of candle may be gauged from the fact that, whilst about 40,000 tons of paraffin wax and 3,000 tons of stearine (as tallow) are used annually in the industry in Britain, the amount of beeswax made into candles does not exceed a few hundred tons.

Spermaceti candles are now made by moulding as in the case of modern candles ; practically their only use is in tests of illuminating power, for which they still form the legal standard of comparison.

Night-lights.—For providing a dim light over a long period of hours, e.g. eight to fourteen hours, special forms of candle material are used which will not burn so rapidly as the ordinary candle. These may be made from pressed tallow of high melting point and good quality or from hot-pressed stearine from distilled coconut oil fatty acids, or from the ordinary paraffin-stearine candle charge. The materials burn slowly with a non-sooty flame and are usually cast in the form of squat cylinders about $1\frac{1}{2}$ inch diameter by 1 inch depth, supplied with a thin central wick specially made for this class of candle, and secured to a small block of tinplate at its lower end in order to maintain the wick vertical throughout the period of burning.

CHAPTER II.—FATTY OILS AS ILLUMINANTS

It has already been indicated that the domestic use of fatty oils for burning purposes in Western Europe has almost died out; large quantities of colza, rape, and some other oils are still used, however, for railway lighting and a few other purposes, and a short summary of the qualities essential in good lamp oils and of the chief types of fatty oils which have been used for this object may be desirable.

The chief aim is to provide an oil which will burn steadily with a comparatively non-smoky flame and which will not adversely affect the wick. The quality of a lamp oil therefore depends equally on its chemical nature and on the impurities which may be present.

As regards the specific nature of the oil, liquid fats which are prone to "gum" or become resinous by oxidation or polymerization are evidently excluded, so that broadly speaking oils of the linseed, soya bean, or even cottonseed types on the one hand, and ordinary whale, fish, and Chinese wood or tung oils on the other, are not desirable, although in the less advanced regions some of these are in fact used. Similarly, not only the solid fats, but also any natural oils which deposit "stearin" at the temperature of use, are of little value.

Consequently the only oils which are really suitable for burning in lamps are liquid fats of a "non-drying" or very feebly drying nature which do not separate solid constituents above, say, 5° C. These include olive, colza, and rape oils in different varieties, possibly castor and ground-nut oils, and expressed oils from cold-pressed fats of the type of lard oil (p. 137).

Naturally the viscosity of the oil is also a factor of some

importance, a value of the order of that of rape oil being the most convenient for most lamp oils.

Assuming that the oil used is one of the class just enumerated, it is further necessary to ensure that certain impurities are not present. The oils must evidently be free from moisture, which will impede smooth burning, whilst traces of soap, mineral matter, or resinous or other mucilage from a crude oil will, if present, be drawn into the wick by capillary action and foul it. Also, substances which might char the wick should be absent and, if sulphuric acid refining of the crude oils has been practised, it is especially necessary to remove all traces of the mineral acid by thoroughly washing the refined oil with hot water before use. Free fatty acidity is also objectionable, since it not only increases the smokiness of the flame, but also tends to char the wick ; burning oils need not be absolutely neutral, but the free fatty acidity should be as low as possible and should not exceed about 2 or 3 per cent. as an outside limit.

The fatty oils actually in use at the present time are probably somewhat as follows :

(i) **Refined Oils in the more Civilized Areas.**—Colza (rape oil) in Britain and Western Europe for railway lighting, etc., and in Eastern Europe as a general illuminant ; olive oil in Spain, Italy, and other Mediterranean coastal regions, and for church sanctuary lamps in Western Europe ; lard oil from pressed edible lard-stearin (p. 137) in the United States of America.

(ii) **Crude or Semi-refined Oils employed in Other Regions.**—Lower qualities of colza or rape oil, especially ravigon oil, are used as general illuminants in Eastern Europe, including Hungary and the Balkans as well as Russia, whilst Jamba rape oil is used in addition to good quality East Indian rape oil in India and the adjacent parts of Asia. Linseed oil is also burned in India and China, whilst Chinese wood or tung oil, although equally a drying oil with linseed oil, is widely used as an illuminant both in China and Japan.

Finally, in Arctic or semi-Arctic regions whale oil

(especially of the sperm variety) and seal oil are still no doubt used to a fairly large extent in the less developed districts for general illumination. Until comparatively recent times lighthouses were illuminated by lamps burning high-grade seal and whale oils, but in the majority of cases at present (at least so far as British practice is concerned) the illuminant is either electricity or more usually an incandescent mantle heated by a kerosene-air mixture.

It will thus be seen that the use of fatty oils as illuminants is becoming extinct in the more sophisticated parts of the world, except in certain cases such as lights on moving vehicles or at isolated points ; it is probable that, with the further utilization of electricity, illumination in these cases will also in process of time cease to be effected either by fatty oils, or by the petroleum substitutes which have already superseded the latter in lamps for domestic lighting.

REFERENCES TO SECTION VI

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SECTION VII.—THE PRODUCTION OF GLYCERINE FROM FATS

Introductory.—The market demand for the glycerine which is liberated during the conversion of fats to soaps, candle material, or fatty acids for other purposes is normally sufficient to absorb the whole of the output. At times, indeed, a glycerine shortage has been threatened, but it is unlikely that this will become serious in future, since, as will be shown in Chapter IV. of this section, means now exist for the manufacture of glycerine from crude sugar if the supply from fat becomes insufficient. Moreover, it is possible that at some later date a direct commercial synthesis from gaseous hydrocarbon sources may become a practical proposition.

The British production of crude glycerine (containing 80 per cent. glycerol) is about 25,000–30,000 tons per annum, whilst the total world production is probably of the order of 100,000–150,000 tons yearly. It comes into trade in four main varieties :

- “*Crude glycerine*”—containing about 80 per cent. of glycerol, coloured.
- “*Dynamite glycerine*”—containing about 95·98 per cent. of glycerol, pale straw-coloured.
- “*Industrial white glycerine*”—made by decolorizing dynamite glycerine, either by filtration through charcoal or by bleaching with a little hydrosulphite.
- “*Chemically pure*” or “*double-distilled glycerine*”—the pharmaceutical product.

Of these qualities, crude glycerine has not been distilled, but is prepared from the aqueous solutions or lyes from fat-hydrolysis by concentration in a vacuum evaporator. The greater part of the crude glycerine made is sold to and distilled by the manufacturers of dynamite or chemically pure glycerine, but a considerable quantity of the best

quality crudes (" saponification " or " autoclave " crudes) is used in some industries, e.g. " anti-freeze " compositions.

Dynamite glycerine, as its name implies, is used in extremely large quantities for the production of nitroglycerine. The latter is of course either mixed with kieselguhr to form dynamite or similar explosives which are mainly used for blasting purposes, or combined with nitrocellulose to give cordite or similar propellant explosives for rifles or artillery. Dynamite or once-distilled glycerine is also used, however, for many other purposes, either *per se* or after a decolorizing process which renders it almost water white. For these ends it is not always essential to employ the best dynamite quality of sp. gr. 1.260 (98 per cent. glycerol), and distillates containing more water are frequently employed (e.g. sp. gr. 1.250=94 per cent. glycerol ; sp. gr. 1.240=90 per cent. glycerol ; or even sp. gr. 1.220=83 per cent. glycerol). The industries which take glycerine of these qualities include toilet soap manufacture, textiles, inks, printers' inks and rollers, duplicating rolls and papers, waterproofing, etc.

" Chemically pure " glycerine represents the highest quality of commercial glycerine and is one of the purest chemicals produced on a large scale. It is almost ash-free, and contains at least 98 per cent. of glycerol, the balance being moisture ; organic matter other than glycerol should not exceed 0.04 per cent., and arsenic, lead, copper, etc., must be completely absent. Glycerine of this kind is demanded in quite considerable quantities for use in medicines and ointments and other forms of pharmaceutical preparations intended for human use either internally or externally.

In the succeeding chapters the technology of each of the foregoing varieties of commercial glycerine is considered in some detail, and the analytical controls of purity applicable to each class of product are described.

CHAPTER I.—CRUDE GLYCERINE

CRUDE glycerine, *i.e.* the aqueous liquors from fat-hydrolysis concentrated (after a preliminary purification from organic impurities) until they contain about 80 per cent. of glycerol, is obtained in the following qualities :

(i) *Soap lye crude*, from the ordinary soapboiling operation in the pan. The soap lyes contain from 3 to at most 7 per cent. of glycerine, and furnish a crude glycerine which may be straw coloured but is more usually full yellow or clear brown in colour. Soap lye crude is produced in greater quantity than any of the other varieties, owing to the predominance of the open pan procedure in fat-saponification, but it contains far more mineral salts (sodium chloride) than saponification crudes.

(ii) *Saponification crude*, better termed *autoclave crude*, which results from the concentration of the “sweet waters” or aqueous liquor from fat-hydrolysis in autoclaves in presence of small amounts of basic oxides (*cf.* p. 271). These “sweet waters” are comparatively free from soap or other organic matter and furnish the best quality of crude glycerine ; a similar pale crude equally free from excess of mineral salts is produced from the aqueous lye resulting from the Krebitz or lime-saponification process, which is used to a fairly large extent on the Continent. The concentrated glycerine lyes from either the autoclave or the lime-saponification processes are therefore frequently classed together in technical practice under the general heading of “saponification crude” ; the original lyes contain up to about 15 per cent. of glycerine, so that the amount of water which must be evaporated to yield the same weight of crude glycerine is, for “saponification crude,” only about

one-third to one-quarter of that in the case of average soap-lye crude.

(iii) *Twitchell crude*, from fat hydrolysed by the Twitchell catalytic process (p. 275), is made from lyes of about the same glycerine content as autoclave crude, but it has not so good a reputation in the trade. Probably this is because the Twitchell process has been employed hitherto mainly on fats of a lower quality than the majority of those which are autoclaved, so that the inferiority is due to the raw fatty material employed rather than to the hydrolytic process. The mineral content of Twitchell crude is liable to be higher than that of good saponification crude from autoclave "sweet waters," owing to the presence of sulphates from the neutralized sulphuric acid which was used to break the Twitchell emulsion, but from raw fatty material of the same quality there seems no reason why Twitchell crude should be much, if any, inferior to saponification or autoclave crude.

(iv) *Fermentation crude*, from the lipase fat-splitting process, is of definitely inferior quality, so far, to either of the foregoing. Its ash content is about equal to that of Twitchell crude, but as a rule it contains notable amounts of albumenoid and mucilaginous impurities, which impart an unpleasant odour and also introduce considerable difficulties with "priming," both during concentration of the crude and in any subsequent attempt to distil it. The concentration of glycerine in the lye from lipase fermentation is even higher than that from the autoclave process.

(v) *Crude distillation glycerine*, from the sulphuric acid saponification process, is the lowest quality met with in the trade. This is unavoidable, owing to the low quality of fats employed, to the intensive action of the concentrated sulphuric acid on the organic matter present, and to the partial destruction of the glycerine present under the conditions of hydrolysis.

Manufacture of Crude Glycerine.—The production of crude glycerine from any of the above types of lye consists essentially of two stages :

(i) Conversion of the lye into a form suitable for concentration.

(ii) Concentration to crude glycerine by removal of water vapour in a vacuum evaporator.

The first stage of the process involves the production of a neutral lye, alkali in soap lyes being neutralized by mineral acid, and sulphuric acid when present in the other lyes being combined with lime or baryta, and the resulting salts removed from the system as precipitates as far as possible. Organic matter, whether albumenoid, mucilage, or fatty acids, is removed as far as possible by coagulation or precipitation with metallic compounds (usually hydrated iron oxide or alumina) and the clarified neutral lye is then ready for concentration.

The second stage of the process is carried out in a double effect or triple effect multiple tube vacuum evaporator, the feed and rate of evaporation being arranged so that the liquor in the first pan does not reach the salting-out point. Salt, however, is precipitated in large quantities in the second pan, and this is collected in a salt box which can be periodically emptied as it fills up without breaking the vacuum on the pan. The final concentration of the glycerine can rarely be effected in a double effect, the pan either working as a single effect pan or else the charge is run out and transferred to a separate single effect evaporator. Solid crystalline salts gradually fall to the base of the vessel and are drawn off into "salting boxes" as described below.

The modifications in the general procedure which are necessary to suit the different varieties of glycerine lyes will next be considered.

Soap Lye Crude.—The lyes from the soap pans (p. 269) are pumped into large tanks and allowed to settle for as long as practicable, soap scum which rises to the surface being taken back to the pans. The settled lye still contains a very small amount of suspended or dissolved soap, and, especially if from a nut oil charge, it will contain in solution as soaps most of the caprylic and caproic acids which were originally present in small amounts in the fat. Also, pro-

ducts of rancidity present in the original fat will have been broken down to some extent into fatty acids of low molecular weight ; although the percentage of these on the original fat will probably have been insignificant, the proportion may become appreciable when measured in terms of the glycerine present.

The settled lyes from a soap pan are also slightly alkaline, and they are therefore boiled in large tanks with a slight excess of hydrochloric acid and a metallic oxide ; hydrated iron oxide is most commonly used on account of cheapness, but basic ferric sulphate or aluminium sulphate (" alumina ferric ") is also widely used. All reagents should be free from arsenic.

The excess of hydrochloric acid is neutralized at the expense of part of the iron oxide, and the ferric chloride so formed interacts with the sodium salts of any dissolved fatty acids producing insoluble iron salts of the latter. The precipitated iron soaps, together with any undissolved hydrated oxide, act as a fairly efficient coagulant or adsorbent for other neutral organic materials of high molecular weight which may be present and thus effect a fairly thorough clarification ; the ferric salts also serve to remove any traces of arsenious salts present. The clarified lye is filter-pressed to remove the iron precipitate, and, after neutralization of the slight excess of acid, is stored in the tanks which feed the evaporators.

The general lay-out of the latter has been described above ; the clarified lyes pass into the first effect (tubular evaporator), which is heated by fresh steam and maintained at a moderate vacuum, the water vapour or steam produced by the evaporation serving as the heating steam in the second effect, where evaporation proceeds at a lower temperature, a considerably higher vacuum (25-27 inches of mercury) being maintained in this section.

Concentration is not allowed to proceed in the first effect beyond the point at which solid salt commences to separate, the objects being to avoid incrustation of the heating tubes and to obtain all the deposited salt in the second

vessel. The solid salt is periodically removed (the " salting box " being opened to air without disturbing the vacuum in the evaporator above) and is centrifuged, when the adherent crude glycerine is removed from it practically quantitatively and the salt is ready for re-use in the soap pans.

The finished soap lye crude still retains in solution, however, about 10 per cent. of its weight of salt ; the presence of an amount of " ash " or mineral matter of this order in crude glycerine indicates at once that the specimen is a soap lye crude, confirmation being afforded by the production of a dense precipitate of silver chloride with silver nitrate solution.

Soap lye crude is usually pale brown in colour, although it may vary from pale yellow to very dark brown. It should possess a slight, not altogether unpleasant, smell from which any odour of a sharp or foetid character should be absent. If the lyes are from very low-grade fat, such, for example, as badly oxidized or fermented whale oil or bone fats, soluble nitrogenous products may be present and also trimethylene glycol, $\text{CH}_2(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2(\text{OH})$, which is formed from glycerol by fermentative change (*cf.* p. 32 and below).

Low-grade soap lye crudes of this kind, however, are avoided as far as possible in practice, since the main outlet for soap lye crude is as a raw material for the production of distilled or dynamite glycerine, from which trimethylene glycol must be absent, whilst the presence of more than traces of the soluble nitrogenous materials causes great difficulty in " priming " and frothing and also leads to an inferior distilled product.

Saponification Crude.—The lyes or " sweet waters " from autoclaved fats and from lime (Krebitz) saponification of fats yield crude glycerine which, if the original fat was of high grade, are equal in colour and odour to the best soap lye crudes and have the advantage of containing an insignificant proportion of inorganic solids.

The " sweet waters " in both cases are feebly alkaline in reaction, due to the presence of lime (or magnesia). This

is rectified by neutralization with hydrochloric or sulphuric acid as in the case of soap lye crude, or by the addition of oxalic acid which removes all calcium as oxalate, hydrated iron oxide being simultaneously added to the agitated solution as a precipitant for traces of dissolved soap and a coagulant for colloidal matter. In order to precipitate as much calcium sulphate as possible when sulphuric acid has been used, precipitated barium carbonate may be advantageously added in the final stages of the clarification process.

The filtered liquor is evaporated in the same type of apparatus as soap lye crude, and furnishes a sweet-tasting crude glycerine which is pale yellow to pale brown in colour and should only contain traces of organic matter other than glycerol and not more than 0·3 per cent. of ash.

Saponification crude is sufficiently pure in many cases to be worth filtering through decolorizing charcoal (*c.f.* Chapter II., p. 436, and Chapter III., p. 447), when the coloured organic matter present is largely adsorbed by the charcoal and an "industrial white glycerine" results which is employed to a considerable extent in place of distilled glycerine in some of the industries mentioned on p. 423.

Twitchell Crude.—Acid water from the Twitchell saponification process contains considerable amounts of sulphuric acid, which is somewhat of a bugbear in glycerine concentration, because when present as calcium sulphate it tends to form a very hard scale on the evaporator tubes, whilst if converted to sodium sulphate it causes difficulties in priming and in separation of the deposited salt, which is much less amenable to treatment than sodium chloride.

The Twitchell acid waters are therefore neutralized first by lime, the process being completed by boiling with barium carbonate, which removes dissolved calcium sulphate as far as possible, by separation of both calcium carbonate and barium sulphate; or the soluble mineral matter may be removed in three stages by consecutive treatment with lime, baryta, and finally oxalic acid. As usual, hydrated iron oxide or a similar material is also agitated with the liquor at this stage in order to secure removal of as much

neutral colloidal impurities as possible and of any fatty acid as soap. Decolorization with charcoal is frequently then employed prior to evaporation of the clarified liquor.

Concentration in the evaporators is somewhat more awkward than in the preceding cases, owing to the presence of small amounts of dissolved salts and, very frequently, of excessive organic impurities due to the original fat having been of inferior quality.

The character of the product obtained depends mainly on that of the original fat hydrolysed: if the latter was of good quality, the resulting Twitchell crude is hardly to be distinguished from saponification crude, although crude from liquors which have undergone any treatment with free sulphuric acid is usually to be distinguished by the possession of a characteristic unpleasant taste. Twitchell crudes owe their somewhat lower grading in the usually accepted scale mainly to the fact that they emanate, more often than not, from greases and waste fats of a low order of purity.

Fermentation Crude.—The acid liquor from the lipase process is held in still lower repute than the preceding, but the quality should improve as the hydrolysis technique is strengthened. However, this type of liquor is almost certain always to contain more colloidal organic matter than the former classes, and, after preliminary neutralization and precipitation as in the case of Twitchell crude, it will probably always be found necessary to pass the filtered clarified liquor through a bed of adsorbent material (decolorizing char) prior to concentration.

The cost of purification will thus tend to be greater than in the other classes, but if the original fat is of fair quality, a fermentation crude should thus be obtainable after evaporation which, although usually dark-coloured, will not contain excessive amounts of ash and organic matter and should be amenable to distillation, especially if mixed off with soap lye crude during the latter process.

Crude Distillation Glycerine.—The liquors from the sulphuric acid saponification process (p. 279), which is

employed almost exclusively upon low-grade fats, give the lowest yield and poorest quality of crude glycerine of any. In many cases it is not worth while to attempt its recovery.

The procedure employed, when glycerine is extracted from these materials, is that followed in the cases of Twitchell and fermentation crudes, namely, neutralization of the sulphuric acid present by lime and baryta in presence of a coagulant, preferably followed by filtration through charcoal.

Crude distillation glycerine is usually of fair colour, but its taste and odour are poor, whilst the organic matter and inorganic solids present are higher than in saponification, Twitchell, or even inferior fermentation crudes. The better grades of this crude can, however, be used to some extent in the manufacture of dynamite glycerine.

The Valuation of Crude Glycerines.—The standards generally accepted for crude glycerine rest on the Report of an International Committee on the analysis of crude glycerine issued in 1911, and the corresponding British standard specifications for soap lye and saponification crude glycerines, approved by the trade in 1912.

The reader is referred, for complete details, to the Report of the International Committee itself or to the very full quotations therefrom in the analytical handbooks of Lewkowitsch, Allen, Elsdon, etc.

Glycerine crudes are sometimes quoted on the basis of the specific gravity, which may vary from 1·23 to 1·30 and is obviously influenced by whether a soap lye crude containing much dissolved sodium chloride or a saponification crude of low ash content is in question.

The International Committee's Report and the British Standard Specifications confine attention primarily to the glycerol content, the ash, the organic residue, and the moisture present. "Experience has shown that in crude glycerine of good commercial quality the sum of water, total residue at 160° and corrected glycerol by acetin test result, comes to within 0·5 of 100. Further, in such crudes the dichromate (glycerol) result agrees with the uncorrected result to within 1 per cent." Discrepancy therefore indi-

cates the presence of trimethyleneglycol ; more recent work on the presence of the latter compound is dealt with below.

For the estimation of *glycerol*, standardized methods for the determination by the acetic and dichromate methods are quoted (these have already been given in Section I., Chapter IV., pp. 65, 66). The "corrected" acetic figure referred to is the apparent amount of glycerol present by the acetic test, less the acetic value of the "total residue at 160°" expressed in terms of glycerol.

The *total residue at 160°* is determined by neutralizing 10 gms. of the crude (diluted in a 100 c.c. flask) with N.HCl until the alkalinity is 0·2 per cent. as Na₂O. The solution is made up to 100 c.c. and 10 c.c. are measured into a weighed flat-bottomed glass or platinum dish 2½ inches diameter by 1 inch depth ; the dish is placed on a steam bath until most of the water has evaporated, and then in an oven at 140° C. until nearly all the glycerine has disappeared. It is then cooled, moistened with 1 c.c. of water and the residue dissolved, and the dish re-heated, first on the steam bath and then at 160° C. for exactly one hour, cooled in a desiccator and weighed. The moistening process with 1 c.c. of water and subsequent operations are repeated in exactly the same manner until a constant loss of only 0·0010-0·0015 gm. is obtained.

The resulting figure, or "total residue at 160°" = organic residue + ash.

The best qualitative test for the presence of undesirable organic matter in crude glycerine is to warm the diluted crude with a filtered solution of basic lead acetate ; good crudes remain almost unchanged, whereas poor quality crudes (*e.g.* a bad fermentation crude or crude distillation glycerine) yield a cloudy voluminous precipitate, more or less abundant according to the amount of colloidal organic matter present.

The *ash* is obtained by weighing out 3-5 gms. of the crude in a platinum dish, slowly evaporating off the glycerine, and finally incinerating the residue at a dull-red heat so that the residual organic matter is charred thoroughly.

The cooled residue is leached with hot water, filtered and washed, and the filtrates are re-evaporated in the dish and finally heated to constant weight at about 250° C.

The *moisture content* of crude glycerine is to be determined by dropping 1·0–1·5 gm. of the sample on to 2–3 gms. of very bulky, purified asbestos in a weighing bottle and plunging the latter in a vacuum desiccator at a pressure of 1–2 mm. of mercury over concentrated sulphuric acid until the weight becomes constant (about 48 hours at 15° C.).

The British specifications give the following standards for these figures, with the limit at which the buyer has a right to reject the parcel :

	SOAP LYE CRUDE.		SAPONIFICATION CRUDE.	
	Standard.	Limit.	Standard.	Limit.
Glycerol	80	78	88	86
Ash	10	11	0·5	2
Organic residue	3	3·75	1·0	2

Lewkowitsch quotes the following values as exemplifying crudes of the various classes dealt with in this chapter :

	Soap lye crude.	Saponification crude.	Twitchell crude.	Fermentation crude.	Crude distillation.
Sp. gr.	1·3	1·240–1·242	1·2415	1·2369	1·240–1·242
Glycerol	80–86	85–90	87·2	—	84–86
Ash	10	0·3	0·5	0·5	2–3·5
Organic matter	1·3	0·5	1·9	1·5	2

Other tests which are prescribed by the International Committee's Report are those for free caustic alkali, alkalinity as carbonate, alkali combined with organic acids, and acidity. "In valuing crude glycerol for certain purposes it is necessary to ascertain the approximate proportion of arsenic, sulphides, sulphites, and thiosulphates."

Arsenic should be completely absent from the crude glycerine, for otherwise it will have become converted into glycerol arsenite, $C_3H_5O_3As$, and this compound is volatile in glycerol vapour and thus cannot be removed in the course of subsequent distillation ; since much crude glycerine is converted into "chemically pure glycerine" for pharmaceutical use, it is highly desirable to exclude sources of arsenic rigorously during the working of any crudes which will possibly form the raw material for medicinal glycerine later. The chief means by which arsenic enters into crude glycerine is in the mineral acids (and to a less extent the

alkali, lime, iron oxide, etc.) which are used in the course of refining.

Sulphides, sulphites, and thiosulphates, when present in crude glycerine, lead to trouble in the distillation and to the presence of sulphur compounds in the distilled glycerine. These impurities may be tested for by the usual methods employed to detect traces of the respective acids. At the time when soda from the Leblanc or black ash process was largely used in the fat industry, these thio-compounds were a frequent source of trouble in glycerine ; since the bulk of the soda employed in the trade has been prepared by the ammonia-soda or electrolytic processes their appearance has been a rare occurrence.

Trimethylene Glycol.—It has already been mentioned that trimethylene glycol, $\text{CH}_2(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2(\text{OH})$, is found in crude glycerine on occasion, and that it is produced from glycerol by fermentation in the case of rancid or low-grade fats which have deteriorated during storage, etc. The production of this material is not confined to glycerol in presence of or combined in fats, for a considerable proportion of the compound formed may arise during the storage of soap or other lyes in tanks. Under these conditions infection of the store tanks by various species of moulds may occur, and acidic, gas-forming and alkaline types of fermentation are described by Rayner, who quotes figures which prove that it is in the "alkaline" fermentation that trimethylene glycol is most abundantly produced from the lyes. This work suggests the advantage of maintaining sterile conditions where possible in the lye-tanks, in order to minimize loss of glycerol by further conversion into the glycol.

Trimethylene glycol can, it is true, replace glycerine for many purposes where the latter acts as an absorbent for water, or to lower the freezing point of water in radiators, etc., and it can be separated from glycerine during distillation of the latter. Since it boils at 210°C . (760 mm.), it is much more volatile than glycerine and condenses for the most part with the "sweet waters" in a glycerine distillation plant (*cf.* next chapter, p. 440). By re-working the

"sweet waters" from a charge fairly rich in trimethylene glycol it is not difficult to obtain the latter in a state of comparative purity.

It is necessary that distilled glycerine for dynamite should be quite free from trimethylene glycol, and the methods given by the 1911 Committee are now recognized to be not sufficiently delicate for the detection of undesirable quantities of the glycol. Thus, if the analysis sums up to 99·5 per cent., and if there is only a difference of 1 per cent. between acetin and dichromate tests, this may correspond to the presence of somewhat over 2 per cent. of trimethylene glycol; further, as the 1911 Report admits, the calculation of the glycol content by proportion between the value found and the theoretical values ("as glycerol") for glycerol and trimethylene glycol is but a rough method of evaluation.

Cocks and Salway have therefore studied this question further, and in 1918 they suggested that if the crude glycerine were distilled in the laboratory under reduced pressure (15–30 mm.) until about 30 per cent. had distilled over, all the trimethylene glycol would be in the distillate, and by determination of the specific gravity and the acetyl value (calculated as glycerol) of the latter its content of glycerol (x) and trimethylene glycol (y) may be calculated from the equation :

$$\text{Acetyl value (as glycerol)} = x + 0.81y$$

$$\text{Specific gravity} = \frac{100}{100 - 0.2082x - 0.0503y}$$

from which the percentage of glycol in the original crude follows.

In a further communication in 1922 they have improved the method further by constructing graphs between the specific gravity and the apparent glycerol (acetin method) contents from determinations of a large number of mixtures of the pure glycol and pure glycerol with water. By use of the graphical method it is stated that the amount of trimethylene glycol in a crude can be ascertained within 0·2 of the actual percentage present.

CHAPTER II.—DYNAMITE GLYCERINE

THE presence of dissolved mineral salts and coloured organic compounds in crude glycerine renders it unsuitable for use in many industries. It is possible, where the only serious objection is the colour of the material, to improve the latter to a very pale yellow or almost colourless state by a bleaching treatment.

The product, which is variously known as "refined," "industrial," or "industrial white" glycerine, is obtained either by filtration of the crude through layers of activated charcoal, by agitation with a small percentage of sodium hydrosulphite or sodium formaldehyde-sulphonylate, or by other methods. This refined quality of crude glycerine is used in the ink and plastic trades, as an "anti-freeze" in motor car radiators, and also to some extent in the production of the transparent soaps and other purposes where distilled glycerine is not essential.

The chief outlets for glycerine, namely, the explosive industry (nitroglycerine) and medicinal and pharmaceutical preparations, require a quality of glycerine which is of a much higher degree of purity and from which all but traces of mineral matter and organic compounds other than glycerol are absent. Also, in the nitroglycerine industry and for many purposes in pharmacy it is necessary to have as little moisture present as possible.

The crude glycerine is therefore submitted to distillation under reduced pressure in a current of superheated steam and the condensed glycerine is further concentrated to an almost anhydrous state by heating in vacuum-pans.

A single distillation of good crude glycerine on a commercial scale usually produces a distilled glycerine sufficiently pure for conversion into nitroglycerine or dynamite, although

not absolutely colourless : this once-distilled glycerine is known in the trade as *dynamite glycerine*.

To obtain colourless glycerine which, except for the presence of about 2 per cent. of water, approximates to the pure compound glycerol, $C_3H_5(OH)_3$, a second distillation (usually accompanied by refining with charcoal or similar means) is necessary ; the twice-distilled glycerine, which is that used for medicine, pharmacy, and edible purposes, is known as *chemically pure glycerine*.

In this chapter we are concerned mainly with the single distillation process whereby crude glycerine is transformed into dynamite glycerine.

Formerly the distillation was carried out by means of an apparatus similar to that used for distilling fatty acids (p. 279), *i.e.* a pot-still heated by direct fire or gas was employed. The charge of crude glycerine was placed in the still, which was connected by a swan-neck to a condenser system, and a current of superheated steam was driven through the heated crude whilst the whole apparatus was evacuated by a pump. This system had the defects of entailing considerable loss of glycerine by decomposition due to local overheating in the still, whilst the regulation of the steam current was difficult and tended to excessive splashing and frothing.

Modern improvements have been directed to securing an even heating of the crude liquor in the still and an even flow of superheated steam under accurately controlled conditions, together with more economical use of the heat supplied, so that the yield of glycerine per unit of coal burnt to supply heat and steam has been notably increased ; at the same time the amount of glycerine recoverable in practice from that originally present in the crude has been greatly improved, whilst the quality of the once-distilled product is much higher than under the old conditions.

A variety of designs of plant for the distillation of glycerine exists at the present time, and these may be illustrated by some account of the processes devised by van Ruymbeke (1893), and Wood (1907 and 1913).

The principal of the van Ruymbeke still has been adopted very widely in glycerine distillation and it is especially adapted to the working of batches of crude, although it can also be conveniently applied to a continuous, or, at all events, a semi-continuous system of working.

Direct firing is completely excluded, the crude glycerine being heated up to the distillation temperature by a coil through which high-pressure steam is passed; the chief improvement made by van Ruymbeke, however, is in the introduction of the superheated steam. If this is admitted directly into the glycerine liquor (which is under a relatively intense vacuum) the expansion of the steam involves a reduction in temperature which causes loss of effective steam for distillation and dilution in the still by the production of condensed water: alternatively, if this is corrected for by additional superheat on the steam or direct heat on the glycerine liquor, temperatures are developed locally which are sufficiently high to cause decomposition of some of the glycerine.

Van Ruymbeke obviated this by delivering the superheated steam into a long coil which communicates freely with, and ends in a perforated discharge pipe in the crude glycerine liquor in the still; this coil is contained in a pre-heater which is heated by the steam (still at the same pressure) from the coil which heats the still-liquor, so that the expanded steam has time to re-acquire the exact temperature of the contents of the still before it reaches the latter.

The distillation portion of a van Ruymbeke plant therefore consists essentially of the following parts:

(i) An expansion chamber (preheater or heat adjuster) in which superheated steam is fully expanded and brought to the exact temperature of the still-liquor as described.

(ii) The still itself, which usually consists of a cylindrical vessel with dished ends containing a closed heating coil supplied with steam from the same source as that which heats the expansion chamber and furnished with an inlet pipe for crude glycerine, a vapour pipe at the top leading

to the condensers, and an outlet at the base for removal of the "still residues" or "glycerine foots."

(iii) The fully expanded steam from the coil or expansion chamber (i) is conducted by a pipe to a perforated distributor near to the base of the still.

The still (and the expansion coil) are in direct connection, *via* the condenser system, with a barometric condenser and vacuum-pump, which maintains an absolute pressure of $1\frac{1}{2}$ to 2 inches of mercury throughout the whole system.

The still is charged to about one-third of its capacity with crude glycerine, evacuated, and the contents heated to about 170 - 190° C. by means of the dry coil (the steam is usually at 180 lbs. per sq. in. pressure, and the temperature attained should be slightly higher than the boiling point of glycerine at the working pressure of the system); super-heated steam is then admitted into the expansion chamber (which has also been brought to the temperature of the still), and passes into the heated crude, at the same temperature as that of the latter, through a series of fine jets. Under these conditions the glycerine is volatilized smoothly and passes away with the steam into the condensers as described below.

Fresh crude may be admitted from time to time until the amount of non-volatile matter ("glycerine foots") increases so far that distillation is hindered; it is then discharged from the base of the vessel and forms a thick dark mass, which still contains a small percentage of glycerine and will also contain varying quantities of poly-glycerols. These are partial condensation products or ether-derivatives of glycerol which are formed from the latter by the action of heat, especially in presence of alkalies. It is therefore desirable to distil crude glycerine which is as nearly neutral as possible.

The glycerine vapours and steam leaving the still were formerly condensed in one stage as completely as possible and the condensate was then re-evaporated under vacuum until it reached the requisite concentration. Later the procedure of fractional condensation was adopted: a

battery of several condensers is employed the first members of which are air-cooled. In these the vapours are more or less stripped of high-strength glycerine which condenses into a receiver or receivers at the base ; the vapour from the hot condenser consists of steam which still contains 10 per cent. or thereabouts of glycerine, and this passes on to condensers cooled by cold water and finally to a barometric condenser. The condensates from the cold condensers are termed " sweet waters," and are re-concentrated with crude glycerine or worked up separately to about 80 per cent. glycerine by evaporation and then re-worked in the still.

Alternatively, the vapours from the still may be passed into the base of a condenser which is constructed on the lines of a plate fractionating column. The lower part of the condenser consists of a series of plates with perforations over each of which a loose-fitting metal cap or dome is mounted, ducts being fitted in each plate to permit the downward flow of condensed glycerine. At the top of the column a condenser is fitted through which water or exhaust steam may be passed, if necessary, to maintain the balance in the column. The bulk of the glycerine is separated in this column by a process of fractional condensation, the latent heat of the condensed glycerine being conveyed to the diluted vapours on each condensation plate. In this way high-strength glycerine is constantly delivered from the base of the column, whilst the vapours which reach the top contain but little glycerine ; these are passed through a cold-water condenser and yield " sweet waters " (dilute glycerine liquor) for re-concentration as in the previous case.

The technical efficiency of the van Ruymbeke still depends on the correct temperature of the steam introduced into the still and the volume admitted, which should be as small as possible consistent with rapid distillation. These factors conduce on the one hand to smooth running and high quality of the product, and on the other hand to economy in fuel, both in respect to the steam consumed in the distillation and in re-working the comparatively small proportion of " sweet waters " produced.

The principle of Wood's more recent method of distillation is directed towards still greater heat efficiency, and depends on the employment of a single stream of superheated steam which is passed through a battery of from four to six stills. The Wood still has become widely used in the United States, but has not yet been used so extensively in this country or on the Continent. This is probably due to the fact that, although its high efficiency is admitted, it involves the construction of a large and complicated plant and so is suited chiefly only to the needs of those distillers who operate on a very large scale.

The principle of the system is that the vapours from steam and crude glycerine in the first still are passed through a fractionating condenser in which they are stripped of the concentrated glycerine condensate ; the uncondensed vapour passes on and becomes the steam provided for the distillation of the crude in the second of the battery of stills, where the process is repeated. In all but the first still the injected steam is provided by the "sweet water" vapours delivered from the condenser attached to the preceding still ; the "sweet water" vapours from the condenser of the final still in the battery pass through a cold water condenser and thence to the "sweet water" concentrators, which are arranged as a double-effect evaporator and coupled to the same vacuum system as the main stills ; the steam from the "sweet water" evaporator usually supplies the first still with free steam for the distillation.

The fractional condensers attached to each of the stills are maintained at 80° by water boiling with a pressure of about 14 inches of mercury ; the steam evaporated from the cooling system by the latent heat developed by the glycerine as it condenses is not lost, but is utilized in assisting to evaporate the "sweet waters" in the second effect. Fresh steam is used to heat the first effect, and the evaporated water vapour from the dilute glycerine is united with the steam from the condensers and provides heat for the second effect, whilst, as already stated, that from the second effect is used to volatilize glycerine from the first still of the series.

The main stills are all maintained under as high a vacuum as possible (at least 2 inches of mercury absolute), and it is evident that if the steam was admitted beneath the surface of a layer of glycerine liquor in each still an appreciable variation in pressure would subsist over the range of stills in the battery. This is obviated by injecting the crude glycerine into the steam in the still in a fine spray, so that equilibration of pressure is secured and also an exceedingly intimate admixture of steam and crude liquor.

The operation of the Wood process may therefore be summed up as follows : Each "still" is connected at its base to a centrifugal pump and crude glycerine in the still is circulated through the pump into a preheater (supplied with superheated steam), whence it is delivered at about 190° C. into the still by means of a spraying device. Here, in the first still, it meets a current of fully expanded steam (from the "sweet water" evaporators), the glycerine is volatilized and separated in the condenser, whilst the "sweet water" vapours pass on as described above to the next still, and after completion of the passage through the battery of stills and condensers are condensed and passed on to the "sweet water" concentrators.

The distilled glycerine is withdrawn at the base of each fractional condenser and is collected either separately or in one outlet. In general it is then ready for use as dynamite glycerine ; or it may be decolorized by passage over or agitation with decolorizing charcoal, or, if not up to strength, may require further concentration in a vacuum evaporator.

A definite proportion of the contents of each still is usually removed from circulation continuously, and this forms the still residues or foots derived from the Wood still. The residues are very similar in appearance and composition to those obtained in the van Ruymbeke plant.

One other form of glycerine distillation process, the Garrigue, may also be referred to ; it combines some of the main principles of the van Ruymbeke still with those of the heat economies of the Wood system, and is considered by some authorities to be in many respects the best of all

glycerine distillation plants. Like the Wood still, its use has so far been mainly confined to the United States.

Fresh modifications in glycerine distillation plant are described or put into operation from time to time. These concern for the most part improvements in the vacua employed (with consequent lowering of temperature in the still and improvement in yield and colour of the distillate), improved methods of continuous operation, removal of salt and still residues, of heating and condensing systems, etc., in order to improve the efficiency of the process and to reduce its running costs. References to articles dealing with this subject are quoted at the end of this section (p. 456).

Glycerine "Foots" or "Still Residues."—The thick, dark still residues from distillation of glycerine as carried out in a modern installation contain a certain amount of unrecovered glycerine together with all the mineral salts and non-volatile organic matter originally present in the crude, as well as any polyglycerols which have been produced during the distillation. The glycerine can be recovered from these, where profitable, by boiling them with dilute mineral acid, when tarry products and a certain amount of lower fatty acids are separated, settled, and skimmed off. The aqueous portion is boiled with lime and baryta to remove sulphuric acid, and the settled liquor is further treated with coagulants in order to remove as much undesired organic matter as possible, and preferably treated with a bleaching agent, either chemical or adsorbent. It is then concentrated and, if possible, disposed of as crude glycerine of inferior quality.

Dynamite Glycerine.—The once-distilled dynamite glycerine should be no more than pale yellow in colour, free from arsenic, lead, lime, magnesia, and alumina, and contain only the merest traces of chlorides and organic impurities; the "total residue at 160°" should not exceed 0·25 per cent. and the inorganic ash 0·05 per cent.

For nitration purposes the specific gravity should be 1·261–1·262, and the glycerine should yield over 210 per

cent. of its weight of clear nitroglycerine, free from flocculent matter, when a sample is nitrated under prescribed standard conditions in the laboratory.

The greater part of the once-distilled glycerine manufactured is used for nitration and conversion into dynamite, cordite, etc. The remainder is sold at specific gravities varying between 1.260 and 1.220 for a variety of purposes, including uses in textile industries, as a lubricant where mineral or other oils are inadmissible (*e.g.* in refrigerating machines and certain types of pumps), in hydraulic presses, for filling gas meters or adding to motor-car radiators as an "anti-freeze", in the paper, ink, and leather industries, in the preparation of plastic materials, etc.

A not inconsiderable proportion of the once-distilled glycerine is further purified and re-distilled in order to produce the "chemically pure" or B.P. glycerine of pharmacy.

CHAPTER III.—PURE GLYCERINE

DYNAMITE or once-distilled glycerine, although comparatively pure, is not sufficiently so to meet the requirements of the British Pharmacopœia ; for this purpose the glycerine must be colourless, practically ash-free and free from organic residue, and free from arsenic, lead, copper or other heavy metals, sugar, polyglycerols, and volatile organic matter.

This quality of glycerine (known in the industry as "chemically pure glycerine") is obtained by re-distillation of dynamite glycerine of good quality. The distillation is generally carried out in a still of the van Ruymbeke type, at as low a pressure as possible and consequently at as low a temperature as can be obtained. The operation of the still does not differ from that already described in the previous chapter, and the condensed glycerine is separated as usual and concentrated if necessary to the strength at which it is to be sold. The latter is usually either sp. gr. 1·26, 1·25, or 1·24 (97–98 per cent., 93 per cent., or 89–90 per cent. glycerol).

Finally it may be treated with charcoal in order to remove the last traces of coloured matter which may still be present.

Decolorizing Charcoal.—A few words may be added here on the various kinds of charcoal at present available for refining glycerine.

Formerly animal charcoal was used, but this had its drawbacks, especially in that calcium and other salts present in the charcoal are freely removed in solution in the glycerine ; moreover, the decolorizing power of animal charcoal is of a low order compared with that of other kinds of adsorbent carbon.

The modern charcoals, most of which go by specific trade names, are produced by processes which are to a certain

extent of a "secret" nature, but the general principles employed are fairly well known. They are almost entirely prepared from vegetable sources by processes which depend on one or other of the following methods :

(a) Destructive distillation of a specific wood fibre, followed by an oxygen activation treatment of the product.

(b) Destructive distillation of sawdust, etc., from specific sources which has been impregnated with calcium chloride or a similar salt, followed by a treatment with boiling mineral acid to remove all inorganic matter.

In the first case it has been established that wood from different vegetable sources yields products of quite varying activity : coconut shell or fibre, birch and spruce shavings apparently produce the most active charcoals, whilst other trees give less useful products. The maximum decolorizing power obtainable after the activation treatment appears to be a function of the original variety of wood distilled.

The carbonization is conducted in retorts at about 700° C. until all volatile matter has been driven off. The "activation" treatment follows, and may consist in heating the charcoal at 800–900° C. in a current of preheated steam containing about 2–10 per cent. of air for a few hours. A certain amount of surface carbon is removed by oxidation, and the decolorizing activity is found to be very much increased when this process has been carried out.

In the other method, the distillation is carried on at about 800–900° C. for about twenty-four hours, after which volatile matter ceases to come away. The products are discharged into water whilst hot and are then thoroughly leached first with boiling water, then with hot aqueous hydrochloric or sulphuric acid, and finally again with water. The washed charcoal is dried and mechanically ground and screened to the requisite size.

The adsorption of colouring matters at the solid charcoal surface, as in similar cases, probably depends more on the structure of the atomic surface layers than on any other factor, although evidently porosity (the general structure being a mass of minute capillary pores) is essential to the

production of maximum surface. The "activation" treatments, however, may be regarded not so much as increasing the porosity, but as removing some of the surface atoms and thus leaving the remainder more exposed and unsaturated; the "activated" carbon surface will thus be similar in character to active metallic catalyst surfaces of the general structure suggested in Section III., Chapter III. (Fat-hydrogenation, p. 243).

The size of particle employed depends upon whether refining is carried out by agitation or filtration. In the former case charcoal of as fine a grade as is consistent with ease of filtration is to be preferred, e.g. a powder which passes completely through an 80- or 100-mesh sieve. If the glycerine is refined by percolation through a bed of charcoal, small granules of about $\frac{1}{8}$ to $\frac{1}{16}$ inch diameter are preferably employed for the bulk of the material, a few inches of finer charcoal being added at the top of the filter-bed.

Applications of "Chemically Pure" Glycerine.— The greater part of the chemically pure glycerine manufactured is used in the medicinal and pharmaceutical preparations to which reference has been made, including not only medicines and ointments but also the compounding of emollient solutions for the skin. A considerable amount is also employed in the export tobacco and snuff industries; addition of a small percentage of glycerine to tobacco assists in the retention of moisture and prevents it from becoming unduly dry on storage.

It is also useful in certain cases in preventing the growth of moulds and bacteria, and finds some application to this end in coating preserved meat and fruits. It is also employed to some extent in the wine, spirit, and brewing trades and is sometimes used as a cold solvent for the extraction of the essential oils (perfumes) from flowers, in place of extraction or maceration with neutral fats or alcohol. To some extent it finds application in specific cases as a sweetening agent, and is also put to a variety of minor uses, mainly in connection with the production of edible or toilet products.

Analytical Examination of "Chemically Pure" Glycerine.—The amounts of the impurities characteristic of commercial glycerine which are permissible in the "chemically pure" quality are as follows:

Total residue at 160° C., determined by cautious evaporation of the sample at 160° C., should not exceed 0·05 per cent.

The inorganic *ash* included in this residue should not exceed 0·01 per cent., and heavy metals or their salts (other than the merest trace of sodium chloride) should be completely absent. Lead, copper, etc., are tested for colorimetrically after addition of hydrogen sulphide solution, which should produce no darkening.

Arsenic should be completely absent; it is detected by the Gutzeit or the Marsh test. The Gutzeit test consists in treating 2 c.c. of the glycerine in a long test-tube with pure arsenic-free zinc and a little dilute hydrochloric acid; the top of the test-tube is covered with a triple layer of filter-paper which has been moistened with a drop of mercuric chloride. A blank test with the zinc and hydrochloric acid is made simultaneously. After each capped tube has stood for ten minutes, the filter-papers are removed and the central layer examined. The paper from the blank test should remain perfectly colourless, whilst that from the glycerine should also be colourless, a faint yellow coloration being an indication that at least 0·000002 gm. of arsenic is present. The Marsh test is still more delicate, and consists in heating the glycerine with pure zinc and dilute sulphuric acid and sweeping the evolved hydrogen by means of a current of arsenic-free carbon dioxide through a heated glass tube; the amount of arsenic can be estimated by the intensity of the mirror of metallic arsenic which is deposited by decomposition of the arseniuretted hydrogen produced in the reaction.

The organic residue should not exceed 0·05 per cent., and this should be exclusively composed of polyglycerols. Lower fatty acids and acrolein should be completely absent; the former are distinguished by their odour, or by the stronger and more characteristic odour of their esters

(which will be produced by warming a sample of glycerine in which they are present with ethyl alcohol and a drop of sulphuric acid), whilst acrolein is tested for by standing with aqueous silver nitrate, when no darkening should take place within twenty-four hours.

Sugars are occasionally used as an adulterant in glycerine, and to detect these a polarimetric examination of the glycerine itself should be made; it should, of course, be completely optically inactive.

If the foregoing impurities are in fact absent, the glycerine consists substantially of glycerol with a small percentage of water and, although the glycerol content can of course be determined with almost equal accuracy by either the acetin or dichromate methods (pp. 65, 66), it is in this case unnecessary to have recourse to chemical methods of analysis, since both the specific gravities and the refractive indices of mixtures of glycerol and water have been carefully determined and tabulated for a series of standard temperatures.

Consequently the glycerol content may be accurately judged by determination either (i) of the specific gravity in a specific gravity bottle or pycnometer (care being taken to avoid absorption of any aqueous vapour by the strongly hygroscopic glycerine during the operation), or (ii) of the refractive index by means of an Abbé refractometer at a standard temperature (12° , 15° , or 20° C.). The determination of refractivity is the more rapid and, in the case of glycerine, is in general also more easy to execute with accuracy.

CHAPTER IV.—THE MANUFACTURE OF GLYCERINE FROM NON-FATTY MATERIALS

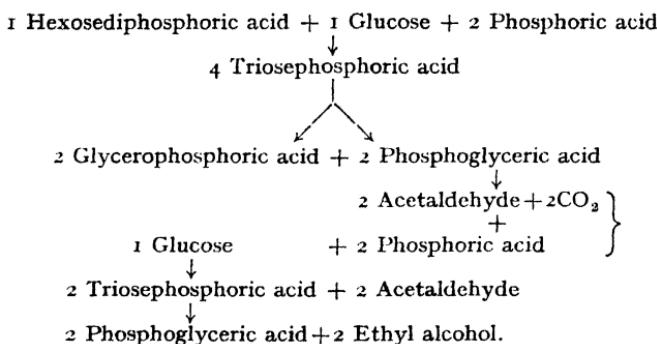
UP to the present time the glycerine market (with the solitary exception referred to below) has been supplied exclusively from fatty sources, and to a large extent the price of glycerine has been under the control of the industries which employ fatty oils for other purposes. In other words, glycerine has so far been solely a by-product, although a valuable one, obtained in the manufacture of soaps, candle material, etc. Naturally this has caused considerable fluctuations in the price of glycerine from time to time, and on occasion the supplies of glycerine available from the fats used in these industries have not sufficed to meet the demand ; this is notably the case during war, when enormous quantities of glycerine are required for the production of propellant and blasting explosives.

The fat industry will not in future, however, be the only source of glycerine, for it is possible to predict at least two sources of the material which are quite independent of its extraction from natural fats, namely, sugar or other carbohydrates, and propylene from hydrocarbon gases.

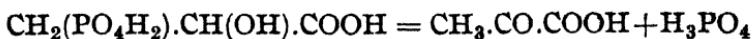
The commercial production of glycerine from sugar is, indeed, an accomplished fact ; during the war of 1914–1918 Germany, being cut off from sufficient imports of fats by the blockade, succeeded in producing glycerine from sugar by fermentation on a scale which is stated to have reached 800–1,000 tons per month. The technical synthesis of glycerine from hydrocarbons has also been effected, although it does not yet appear whether glycerine from this source is likely to be producible at a cost approaching that of glycerine from either fats or sugar.

Glycerine from Sugar.—This process is a controlled form of the ordinary fermentation of glucose or fructose by yeast. Pasteur established the normal presence of 2 or 3 per cent. of glycerine in the ordinary products of the alcoholic fermentation of sugar many years ago, but an explanation of the means by which it is probably formed was lacking until the investigations of Neuberg, followed later by those of Embden and of Meyerhof.

The Embden-Meyerhof explanation of yeast fermentation can be summarized in the following scheme :



Neuberg believed alcoholic fermentation to involve preliminary resolution of glucose into two molecules of methylglyoxal, $\text{CH}_3.\text{CO}.\text{CHO}$, which gave glycerol and pyruvic acid, $\text{CH}_3.\text{CO}.\text{COOH}$, by further interaction with the elements of water. He established that pyruvic acid is converted into acetaldehyde and carbon dioxide by a specific enzyme, carboxylase. The later physiological studies of Embden and of Meyerhof have shown that whilst pyruvic acid, as suggested by Neuberg, occupies a pivotal position in the sequence of actions leading to acetaldehyde and thence to alcohol, it arises from phosphoglyceric acid and not from methylglyoxal (the production of which is now known not to take place) :

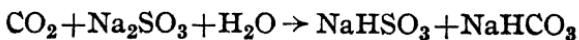


Inspection of the processes involved in the scheme summarized above will show that in normal alcoholic

fermentation, after initial formation of glycerophosphoric acid and phosphoglyceric acid (the latter yielding pyruvic acid and then acetaldehyde), the production of alcohol depends on continuous interaction between acetaldehyde so formed and more triosephosphoric acid. If the acetaldehyde is removed (as bisulphite compound, or by decomposition by alkali), this sequence of reactions is interrupted and, instead, the triosephosphoric acid is continuously transformed into glycerophosphoric acid and phosphoglyceric acid. Glycerophosphoric acid, $\text{CH}_2(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2(\text{PO}_4\text{H}_2)$, thus accumulates in equivalent amount to the acetaldehyde fixed by sulphite or alkali, and ultimately yields glycerol by hydrolytic removal of the combined phosphoric acid.

The technical production of glycerine from sugar by modified fermentation with yeast was found to be quite practicable by the Germans Connstein and Lüdecke, who conducted the fermentation in presence of sodium sulphite, and by the American chemists Eoff, Linder, and Beyer, who employed a special growth of yeast (*Saccharomyces ellipsoideus*) in a dilute alkaline solution (sodium carbonate, borate or phosphate).

In the German sulphite process, a 10 per cent. solution of glucose or cane sugar containing neutral sodium sulphite equal in amount (as anhydrous salt) to 40 per cent. of the sugar present is fermented in the usual plant with ordinary brewer's yeast (*S. cerevisiae*). The action is slower than under ordinary conditions and requires about 48–60 hours at 30° C. for completion. The carbon dioxide formed at first interacts with the sodium sulphite to form an equilibrium mixture of sulphite, bisulphite, and bicarbonate :



When equilibrium is attained (neutral sulphite still being present), the remainder of the carbon dioxide is evolved in the gaseous state.

The yeast can be filtered and used again, providing that intermediately it is employed in a normal fermentation under feebly acid conditions ; fresh yeast is then obtained by

reproduction of the yeast cells, whereas during the sulphite or alkaline fermentations no yeast growth takes place.

The filtered mash is treated with lime and calcium chloride in order to remove the sulphite and carbonate present, and is preferably further clarified with a coagulant such as basic lead acetate, alumina ferric, or charcoal, in order to remove the somewhat abundant non-volatile and hydroxylated by-products.

The clarified liquor is first of all distilled in a fractionating column in order to recover the aldehyde and alcohol produced; the residue from this distillation is then concentrated to crude, and distilled in order to produce dynamite glycerine by the methods described in Chapters I. and II. of this section.

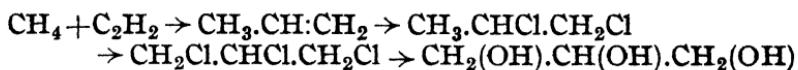
Connstein and Lüdecke state that 1,000 kg. of sugar furnish 230–255 kg. of dynamite glycerine, 240–270 kg. of alcohol, and 95–100 kg. of acetaldehyde. The statement has also been made that, with crude molasses as raw material, sufficient alcohol and aldehyde is obtained from the process to cover the working costs, so that the glycerine recovered represents clear profit. Nevertheless the sugar fermentation process did not secure any foothold against fat glycerine after the termination of the war in 1918.

The alternative American method is carried out somewhat similarly to the sulphite process, but it is recommended that a special variety of yeast, *S. ellipsoideus* var. *Steinberg*, should be employed, and the alkaline salt is added gradually. Thus, a 17 per cent. sugar solution may be fermented at about 30° C. with the yeast, sodium carbonate equal to 1·25 per cent. of the sugar present being added, and further additions of the carbonate made as the fermentation increases in rapidity until the total amount added is equal to 5 per cent. of the original sugar; small quantities of ammonium chloride, potassium phosphate, and magnesium sulphate are also added as nutrients for the yeast. The fermentation requires four or five days for completion and the mash is then filtered, boiled with lime and also coagulating agents and worked up as in the case of the sulphite liquor.

No acetaldehyde is produced by this process, but the discoverers state that a yield of 20–25 per cent. of glycerine is produced, about half of which is recoverable as dynamite glycerine. The yield of alcohol is about 30 per cent. of the sugar consumed. The amount of non-volatile organic matter present in the fermented product is somewhat larger than in the case of the sulphite method, namely, about 20–25 per cent. by carbonate fermentation as against about 15–18 per cent. by sulphite fermentation.

Either method could, however, be employed effectively if necessary on a large scale in the improbable event of a shortage of glycerine from fatty sources.

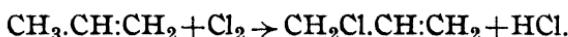
Glycerine from Hydrocarbons.—The synthesis of glycerine from methane and acetylene was claimed in a patent by Heinemann in 1913. It was proposed to obtain propylene by passing methane and acetylene at a high temperature over a catalyst, and then to chlorinate the propylene, obtaining by addition of chlorine $\alpha\beta$ -dichloropropene, which by further chlorination in ultra-violet light should yield $\alpha\beta\gamma$ -trichloropropene, from which glycerine results by transposition with caustic alkali—



The union of acetylene and methane has certainly not yet been achieved in this manner on a technical scale, but nevertheless propylene is known to occur in extractable quantities in the natural gas from petroleum fields, in the gases from petroleum “cracking” stills, and in coke oven gases.

The commercial production of glycerine from propylene has been successfully worked out in the United States by the petroleum industries there, who have been very active during recent years in seeking for new outlets for the various paraffins and olefines of low molecular size which are present in the large volumes of gas available from “cracking” operations. The propylene may be converted into 1,2,3-trichloropropene, and the latter hydrolysed to glycerol, but this hydrolysis proceeds with difficulty. Apparently a

more convenient route is to convert propylene, in the first instance, into allyl chloride and to hydrolyse the latter to allyl alcohol which, with hypochlorous acid, may be transformed to glycerol *via* the moro- or di-chlorohydrins :



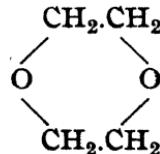
Careful control and attention to conditions is requisite at each stage of this synthesis.

Even when run in conjunction with an electrolytic plant whereby the sodium chloride produced in the hydrolysis is continuously reconverted into caustic soda and chlorine, it would seem that the cost of synthesizing glycerol from propylene would normally be higher than that of producing it from fats. Nevertheless, it is now possible for petroleum or coal to form, if necessary, a third class of basic raw material for glycerine in addition to fats or molasses.

Ethylene Glycol.—Mention may also be made here of this substance, which is a possible competitor with glycerine from fats. It can be produced technically from ethylene, either by combination with hypochlorous acid, when ethylene chlorohydrin is formed, or by union of the gas with chlorine, yielding ethylene dichloride. Either halogen compound can be converted into the glycol, which (at all events in America, where there are abundant natural and artificial sources of ethylene) is apparently on the verge of production at a price not far removed from that of glycerine.

The dinitrate of glycol is said to be as useful in explosives as nitroglycerine, with the additional advantage of conferring non-freezing properties upon substances with which it is mixed, whilst glycol itself may be found capable of replacing glycerine in many of the uses of the latter.

The cyclic ether of ethylene glycol, dioxan



is also now produced commercially, and has excellent solvent

properties for many compounds such as resins, dyes, practically all vegetable and mineral oils, including blown and polymerized fatty oils ; it is immiscible with glycerine.

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SECTION VIII.—THE USE OF FATS AND WAXES IN PAINTS, VARNISHES, AND OTHER SURFACE COVERINGS

A NUMBER of the more unsaturated fatty oils possess the dual properties of thickening by a process of polymerization and of absorbing oxygen with the formation of solid, colloidal, clear solutions. These properties are utilized on an enormous scale when these oils, more especially linseed oils, are employed as vehicles for white or coloured pigments, or for gum-resins and other materials in paints and enamels or varnishes.

Further oxidation or polymerization of the same raw materials produces plastic materials varying in consistency from thin jellies to tough rubber-like, but crumbling, solids, which can be combined with fibrous material to give coherent masses.

Viewed from another standpoint, we may consider the uses of fatty oils (i) for covering rigid surfaces and (ii) for combination in one way or another with fibrous materials in the production of various serviceable commodities. In the present section the parts played by fatty oils in surface coverings will be discussed, and in the next section their functions in the linoleum, textile, and leather trades will be dealt with, these being the cases in which the fats are combined with the fibres of the material rather than applied to the final surface.

The branch of surface coverings includes paints, enamels, varnishes, and polishes : in all but the last instance the components with which we are more particularly concerned are the fatty oils, but in polishes the latter are replaced by the waxes. It is quite beyond the limits of this volume to

attempt any detailed description of the manufacture of the many varieties of each of these coverings, nor is it necessary, since the technology of this side of the subject is amply covered elsewhere (*cf.* sectional bibliography, p. 495).

The description of the rôle of the fatty or "drying" oils in paints, enamels, and varnishes is rendered complicated by the fact that these undergo the complex and still too little understood changes of oxidation and polymerization during the application and maturing of the film. In order to develop the subject as clearly as possible, it has been thought best to deal first of all with the theoretical aspects of these changes, and then to proceed to some account of the manufacture of thickened ("stand"), boiled, and oxidized or blown oils, the latter including not only oils for paints but also some of the products which are combined with fibrous or textile materials, as described in Section IX. The fats and waxes which enter into the composition of most paints, enamels, varnishes, and polishes can then be more adequately described so as to indicate their contribution to the final effects obtained.

The use of "drying" oils in varnishes, enamels, etc., has been increasingly supplemented, and to some extent replaced, by that of new forms of synthetic resins. So many of the latter have become important technical products, and their functions have so much broadened (from constituents of the paint coverings of fabrics such as wood or metal to moulded substitutes for the latter in interior house decoration, or, for instance, for motor car, electrical and other fittings), that they are now treated as an individual branch of technology—the division of plastics. Of the wide range of synthetic resins available as plastics, the phenol-formaldehyde group (bakelite, laccain, novolak), the urea- and thiourea-formaldehyde group, the older cumarone and indene resins, nitrocellulose derivatives for lacquers, the glyptal or alkyd resins (from glycerol, glycol or their mono-alkyl ethers condensed with phthalic anhydride) and the newer class of polymerized vinyl acetate resins may be mentioned as illustrations. In the first edition of this book

some of these were discussed in somewhat more detail, but the subject of plastics has become so large that it now appears inappropriate in this volume to attempt to consider the synthetic resins at any length except in the few instances in which unsaturated fatty oils or acids enter into their composition.

CHAPTER I.—THE “DRYING” AND POLYMERIZATION OF FATTY OILS

Two distinct processes occur in oils of the type of linseed or tung oil when these are exposed to heat and to the action of atmospheric oxygen, and both processes contribute to make such oils (especially the two mentioned) the most suitable fatty vehicles for pigments (paints) and for gum-resins (varnishes). The changes in question are :

(i) A thickening of the oil, which may proceed in certain cases to the extent of transformation into a jelly (gelation), which is undoubtedly due to some kind of association or polymerization of the fatty molecules ; this occurs when the oil is heated for some time to a temperature of about 260° C., and takes place during the production, for example, of “boiled” linseed oil by the old fire-heat process.

(ii) Conversion of the oil into a solid rubbery mass or, in thin layers, a clear hard solid surface, by an oxidation process. This is effected by addition of oxygen to the unsaturated glycerides without any great amount of molecular disruption. Those oils which readily absorb oxygen from the air at the ordinary temperature and become covered with a solid film of oxidation product are known as “drying” oils.

Whether oxidation or heat treatment, or both, have been utilized in the course of adaptation of drying oils for paints or other surface coverings, the polymerization actions referred to under (i) play an important part in the final stages of the process. This chapter is devoted to a brief survey of what is at present known with regard to the chemical and physical mechanisms concerned in both the oxidation and the polymerization of unsaturated fatty oils.

In Chapter II. of this section the production of "stand," "boiled," and "blown" drying oils is dealt with, and it must there be borne in mind that in most of these technical operations both of the above changes are simultaneously involved to a greater or less extent. In order to have a clear understanding of what goes on in the formation of a paint or varnish film, however, it is essential to consider the phenomena quite separately.

Atmospheric Oxidation ("Drying") of Fatty Oils.—The absorption of oxygen by linseed oil, either alone or in presence of certain metallic salts known as "driers," has been repeatedly investigated by numerous workers. References to the more important of their published results will be found in the sectional bibliography (p. 495), and the original papers should be consulted by those who require more complete information on the subject than considerations of space permit here.

The most relevant data are as follows :

(i) Linseed (or other unsaturated fatty) oil absorbs oxygen on exposure to air alone, at first very slowly and subsequently much more rapidly, the rate then progressively diminishing as the process nears completion. At ordinary temperatures the slow "period of induction" may be from one to three days, the process being complete in about 20–30 days; at 100° C. the whole process occupies only 6–7 hours, the induction period being less than half an hour.

(ii) Linseed oil fatty acids behave exactly similarly to the glycerides, but absorb oxygen somewhat more rapidly. The physical nature of the oxidation products from the free acids, however, does not render them adaptable to technical use; hence in practice the glycerides or natural fatty oils are always employed as such in paints, varnishes, etc.

(iii) If small percentages (about 0.1–0.3 per cent. as metal) of certain salts such as lead, manganese or cobalt linoleates or resinates (abietates) are present in the linseed oil the period of oxidation is greatly shortened; this is mainly due to the fact that the induction period is eliminated and oxygen absorption sets in at once at its maximum rate.

(iv) Many of the earlier results were obtained by observation of the increase in weight of the oil film, and led to a maximum observed oxygen absorption of about 18-20 per cent. of the original weight of the oil. Coffey showed that this was lower than the true oxygen absorption value and represented merely the algebraic maximum of the increase in weight due to oxygen absorption, less subsequent diminution due to escape of volatile products of decomposition. He was able to show that the true oxygen absorption was about 28.7 per cent. of the original weight of the oil and that, as earlier workers had believed, the primary process was one of addition of a molecule of oxygen at each ethylenic linkage.

(v) The proportion of volatile products of oxidation is in no case very large, and undoubtedly the constituent to which a paint film owes its peculiar tenacity and transparency is the addition product of the unsaturated glyceride with oxygen, after it has undergone further isomeric and polymeric changes.

(The oxidized product from linseed oil is frequently termed *linoxyn*, but this refers more often than not to the final material obtained, which is a by no means simple mixture of organic compounds ; in its simplest terms it must be looked upon as a conglomerate of unsaturated glycerides which have partially or completely undergone addition of a molecule of oxygen at each double bond (with further transformation of the initial product), together with the unsaturated glycerides which have not been attacked, any mixed saturated-unsaturated glycerides originally present in the oil and perhaps small amounts of other compounds formed by slight decomposition and further oxidation of the first oxygen-addition products.)

Oxidized linseed oil, or "linoxyn," has certain physico-chemical resemblances to the typical colloid gelatin. For example, the viscosity relationships of "linoxyn" and of gelatin are qualitatively similar and both materials swell when treated with suitable liquids (water in the case of gelatin, and hydrocarbon solvents in the case of "linoxyn").

It is at present widely held that the "linoxyn" consists physically of a solid lattice-work of oxidized and polymerized glyceride molecules enclosing the liquid (unchanged) glycerides, the whole forming a perfectly homogeneous solid jelly.

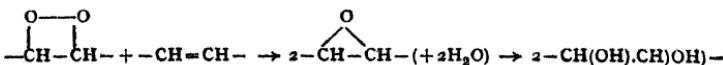
Most "drying" oils other than linseed oil do not give so satisfactory a film on exposure to air; linseed oil itself, if intensively oxidized (*cf.* Section IX., Chapter I.), becomes thick and finally crumbles into soft fragments. In these cases separation of the colloidal solid phase from the homogeneous medium has taken place, and instead of a clear solid film or jelly there is produced a more or less coagulated and heterogeneous system of colloidal solid interspersed with clear jelly.

A few words must be added on the chemical changes which take place during the "drying" of linseed and similar oils, so far as these have been elucidated.

There seems little doubt that the initial product is of the nature of an organic peroxide—indeed it shows typical peroxide reactions such as the liberation of iodine from acidified iodide solutions; on the other hand, the evidence seems to show that the peroxide is only a transitional phase and does not exist to any degree in the final product.

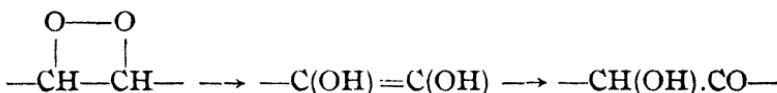
Many schemes have been put forward in the endeavour to account for what takes place subsequent to the initial peroxide phase, some of which can be ruled out more or less completely. For example, no great amount of molecular disruption occurs, otherwise acids and aldehydes of comparatively low molecular weight would be produced, and these are readily capable of detection. The acid value of a "drying" oil increases slightly, but to no very marked degree, during absorption of oxygen.

Again, only minor proportions of the highly crystalline and readily characterized di-, tetra- or hexa-hydroxystearic acids are produced during the oxygen-absorption process, so that such a change as that represented by the scheme



is most unlikely to occur. It has been suggested, incidentally, that hydrogen peroxide itself is produced during the "drying" process and that this acts as an autocatalyst; since hydrogen peroxide converts unsaturated fatty acids or their glycerides into derivatives of the polyhydroxystearic acids, it seems unlikely that this agent plays any part in the formation of "linoxyn."

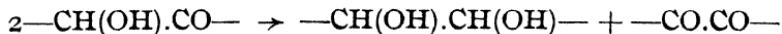
When discussing oxidative rancidity (Section IV., Chapter VII., p. 330) it was mentioned that G. W. Ellis in 1925 put forward the view (foreshadowed earlier by Fahrion) that the peroxide isomerizes into an α -hydroxyketone (ketol) :—



In 1929 Morrell and Marks studied the products present in air-oxidized films of β -elæostearin (the stable isomeric form of the α -elæostearin present in tung oil). By methylation and subsequent fractional distillation of the resulting methyl esters *in vacuo* they were able to show that two of the three conjugated double bonds of elæostearic acid had been oxidized, that the bond ($\Delta^{9:10}$) "near" to the carboxyl group had in fact undergone the transformation suggested by Ellis and was acidic in character, and that the "remote" peroxide ($\Delta^{13:14}$) is basic and much less stable, does not isomerize to ketol derivatives, but readily takes part in polymerization of the oxidized fatty acid molecules. Again, in 1936, Morrell and Davis showed that maleic anhydride forms a diene "adduct" with α -elæostearic acid at the $\Delta^{11,13}$ -bonds, leaving the Δ^9 -bond ethenoid, whilst with β -elæostearic acid it yields an adduct at the $\Delta^9, 11$ -bonds, leaving the Δ^{13} -group ethenoid. The adduct with the $\Delta^{9:10}$ -ethylenic linking oxidizes to a ketol ($-\text{CH}(\text{OH}).\text{CO}-$) compound, whereas that with the $\Delta^{13:14}$ -ethylenic linking gives on oxidation a peroxidic derivative which undergoes polymerization. These observations, whilst substantiating the formation of ketol derivatives, suggest that the peroxide form rather than the ketol form of the oxidized glycerides

is the one which takes the predominant part in any subsequent polymeric changes in the oxidized product. Later observations on this subject have been contributed by Morrell and Phillips, and their experimental data have been mainly instrumental in establishing our present knowledge—still inadequate—of the later phases of the mechanism of atmospheric oxidation of unsaturated fatty oils.

The intervention of the ketol derivatives in the sequence of reactions is probably the cause of some other properties of oxidized oils. Thus, certain "dried oil" films, especially from the more unsaturated fatty oils which contain a good deal of triethenoid (linolenic or elæostearic) glycerides, are apt to develop a yellow colour (which may bleach again on prolonged exposure to air). This yellowing is now believed to be due to diketo-derivatives, —CO.CO—, produced by further oxidation of the ketol compounds present. Moreover, as already mentioned on p. 463, subsidiary amounts of dihydroxystearic acids, etc., have been found in oxidized oils, evidently as by-products, and it is now known that, by a process of intermolecular oxidation and reduction, both dihydroxy- and diketo-compounds can be simultaneously produced from ketols :—



Some further remarks may be interpolated with regard to the "period of induction" noted in the onset of atmospheric oxidation of most of the raw unsaturated vegetable oils. It has already been mentioned (Section IV., Chapter VII, p. 332) that this phenomenon is now ascribed to the presence in the crude oils of traces of complex organic compounds, in the presence of which atmospheric oxidation of the unsaturated fatty groups is suppressed or, at least, much retarded. The possible character of these natural "antioxygenic" materials, and the ability of certain simpler synthetic compounds such as hydroquinone to retard the "drying" of oils (*i.e.* develop in them a prolonged "induction period") was described in Section IV. (*loc. cit.*). In the modern view, the function of metallic

or other "driers" is as much the destruction of compounds in the fatty oils which protect the latter from oxidation, as to provide an actual catalyst of oxidation (a "pro-oxidant"). That the natural antioxygenic compounds (present in the developing endosperm of the ripening seed) play a very important part in the stabilization of natural fats as they are being formed in the fruit is evident when it is recalled that experiments on various species of plants have shown that the most highly unsaturated components of the seed oils are produced in the later stages of ripening of the seed—that is, at a time when the latter is losing moisture and increasingly exposed on all sides to access of air.

Polymerization of Fatty Oils.—Having considered the mechanism of atmospheric oxidation of unsaturated fatty oils, so far as the more evident results of experimental investigation take us at present, we pass to the other aspect, namely, the aggregation or polymerization of unsaturated glyceride molecules, either by some action involving the ethenoid groups themselves, or the latter after they have been transformed into oxygenated derivatives—peroxides, ketols, and so on. In this division there has been an excessive amount of theorizing without sufficient experimental basis, and there has also been considerable experimental study undertaken, which has demolished some hypotheses and developed others on sounder foundations; but nearly all the experimental work has been so far devoted to the problems connected with polymerization by heat alone, and without concurrent or precedent oxidation. There is thus still little definite to say about the structure of a polymerized oxidized unsaturated oil, and the next few paragraphs deal almost wholly with the results obtained by the investigation of thermal polymerization.

Here once more it is simplest to commence with a description of the behaviour of linseed oil (or esters of its component acids) when heated in absence of oxygen at temperatures approaching 300° C. Under these conditions, the iodine value commences to fall rapidly, *i.e.* a certain number of the ethylenic linkages become saturated, not by

addition of hydrogen or oxygen, but by some kind of polymerization effect. When the iodine value has fallen to about 100 ("thin stand oil") the density has increased from about 0·935 to 0·966, whilst the oil has become somewhat, but not very greatly, more viscous. When heating is continued at the same temperature, the iodine value declines further but not so markedly; but the viscosity increases very rapidly and the oil becomes very thick, although still quite clear. Certain oils, notably China wood (tung) oil, proceed further and become converted into a gelatinous or rubber-like material.

The effect of heat is thus to diminish the iodine value (unsaturation) and to increase the viscosity, but the latter effect is most pronounced during the latter stages of reduction of the iodine value; the specific gravity increases as the iodine value falls, the amount of linolenic acid present declines almost to zero (*v. infra*, Table), but in absence of air there is no oxidation. Typical figures for various commercial polymerized linseed oils are given by Leeds as follows:—

	Per cent. loss on thickening	Sp. gr. (15° C.)	Iodine Value	Oxidized acids	Hexa- bromides	Sap. Val.
Raw oil	..	—	0·9321	169	0·3	194·8
Thin oil	..	3	0·9661	100	2·5	196·9
Middle oil	..	6	0·9721	91	4·2	197·5
Strong oil	..	12	0·9741	86	6·5	190·9

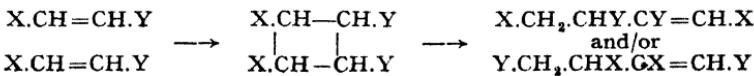
The changes indicated above for linseed oil occupy many hours, but oils which contain a conjugated triethenoid system, such as tung or oiticica oils, behave quite differently, and in the course of a few minutes (9–10 minutes in the case of a good genuine tung oil) the oil passes into a stable colloidal gel solid at the ordinary temperature. Moreover, the amount of conjugated unsaturation present in either a thickened (stand oil) or a completely gelled tung oil is very much less than that of the original oil, and it is thus reasonable at once to postulate that the polymerization has involved interaction or union at the conjugated unsaturated groups.

Within the last few years means of assessing quantitatively the proportion of conjugated unsaturated acids or glycerides present in an oil have been devised: the "diene" or maleic anhydride value (based on Diels-Alder condensation of maleic anhydride with a conjugated system of ethenoid bonds) and absorption spectra (*cf.* Section I., Chapter IV, p. 54). The maleic anhydride value does not discriminate between conjugated diene and triene systems, but the intensity of the absorption bands at $230m\mu$ (diene conjugation) and at $270m\mu$ (triene conjugation) gives a measure of the amount of each type of unsaturation which may be present.

Now, whilst tung oil, in the few minutes at 290° prior to complete gelation, passes through stages of thickening (or "stand oil" formation) comparable with the stages of linseed oil stand oil production, heat treatment of linseed and similar oils, or of the esters of their component di- or tri-ethenoid acids, has been shown fairly conclusively to be accompanied by the development of a small proportion of conjugated unsaturated compounds: the "diene" value tends to increase somewhat and, more positively, the absorption bands at 230 and $270m\mu$ characteristic for di- and tri-ethenoid long-chain aliphatic conjugation appear to a certain extent (Bradley and Richardson). Steger and van Loon, examining by fractional distillation the products of heat treatment at 290° for 15 hours of ethyl linoleate, observed the presence of about 5 per cent. of a conjugated octadecadienoate, probably produced continuously, but relatively slowly, and then more rapidly transformed into polymeric (mainly non-distillable) products. It has thus come to be considered most probable that the polymerization by heat of linoleic or linolenic groups is preceded by the rearrangement of their separate ethenoid bonds to conjugated unsaturated linkings.

The nature of the polymerides produced has naturally also been the subject of much study. The greater part of a heat-polymerized oil is very complex in character: for example, Waterman and Oosterhof passed a thick linseed

oil stand oil through a "molecular still" at extremely low pressure and obtained about 30 per cent. of distillate of molecular weight about 760, which contained much of the saturated and oleic acids from the original oil and was still mainly monomeric, but the 70 per cent. of completely non-volatile oil had an average molecular weight of about 3500. Working with individual esters which have been heat-polymerized, several investigators, by ordinary vacuum fractional distillation methods, have isolated cyclic monomeric compounds, and also dimeric forms, from unsaturated compounds such as elæostearic, linoleic and linolenic acids. The cyclic monomers appear to contain C₆ rings formed from a conjugated triene grouping, but the structure of the dimerides, which may or may not be cyclic, is less certain. It is possible for a six-membered ring to be produced from the conjugated systems of two unsaturated acyl groups or, less likely, that the relatively unstable cyclobutane ring is produced, or, again, a much larger ring containing perhaps 10 or 12 carbon atoms. The first suggestion is perhaps most probable, but Morrell's alternative of rearrangement of an initially-formed cyclobutane ring has also some attraction :—



Whatever the true explanation of the structure of the cyclic monomerides and of the dimerides produced, it is evident that the polymerization proceeds much further than this, and that the final colloidal or gel substances produced are built up from more than two unsaturated groups. At the same time, it is here necessary to distinguish between the union of two molecules of (conjugated) unsaturated acids or of their simple esters, and that of such groups when present in triglycerides. In the former case, the result of dimerization would be to produce a compound of molecular weight about 600 from one of half this molecular size. With triglycerides, two cases arise: (a) union between two acyl groups in the same triglyceride molecule would

involve no increase in its molecular weight (about 850), whereas (b) union between two acyl groups in two different triglyceride molecules would double this molecular weight and produce a compound containing essentially six long-chain acyl groups, some or all of the remaining four of which might still be capable of further polymeric union with other acyl groups in the same, or yet other, molecules.

Even on the basis of the experimental evidence now available (of which only a very condensed résumé has been given) it is clear that there is room for divergence of views and for multiplicity of hypotheses as to the nature of the most complex part of the final products of heat polymerization of unsaturated oils. We shall only mention here some of the general lines of thought which appear to command most attention at the present time. From the physical standpoint there may well be two types of polymers present : (a) a plastic non-oriented structure held by cohesional or van der Waals' forces and (b) a fibrillar, oriented structure dependent on links of a chemical nature (Wornum) ; the two varieties might correspond with straight-chain molecules and with molecules in which condensation has occurred by cross-linking. At the same time, the results of practically all the experimental studies (including those briefly outlined above) lead to the conclusion that changes of a structural character involving ordinary chemical reactivity account for the earlier stages of alteration of a drying oil by heat (isomerization to conjugated systems, conversion of the latter to cyclic monomerides or dimerides by "diene syntheses" or otherwise) ; whilst the subsequent stages, in particular the transition from a very viscous fluid to a solid colloidal gel, may be mainly, or partly, conditioned by forces of a "capillary" or van der Waals' nature set up between the residual unsaturated groups of the chemically-polymerized complexes (Bradley, Kappelmeier, Rossmann).

Kienle, who has discussed the question of polymerization in its general applications to synthetic resins, considers that the heat-thickening of drying oils follows the same general principles and, with Bradley, has stressed the number of

different functional or potentially functional factors which may be concerned in this process. These investigators also regard the main processes as primarily chemical in character, the later stages also being affected by association dependent on the molecular architecture of the polymerides. Here it should be emphasized that the process is clearly a three-dimensional one and cannot be adequately pictured in two dimensions (*i.e.* by formulæ on a plane surface). Whilst fuller understanding of the three-dimensional space features involved demands a more complete knowledge of the spatial structure of the unsaturated triglycerides than we have at the present time, it is reasonable to picture the possibility of some degree of physical aggregation by mechanical interlocking set up between the long-chain acyl groups in two or more of the chemically polymerized molecules. The possible production in this way of a condition resembling a "log jam" (wherein a few logs can interlock and hold up a large number of floating logs of wood) may have some relation to the final formation of rigid gels from the conjugated unsaturated fatty oils (Kienle, Rossmann).

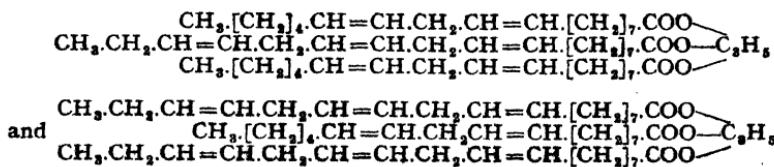
Some General Conclusions.—The changes which occur both in the atmospheric oxidation and in the polymerization of "drying oils," it will be gathered, are still only partially understood, although considerable progress in this direction has been achieved during the past ten or fifteen years. It seems not improbable that a completely satisfactory understanding of the question will only be reached when it is possible to isolate and determine the structure of actual constituents of the final mixture of polymers; so far, this has only been achieved (and here, to some extent only partially) in the case of the mono- and di-meric constituents, which are certainly not those responsible for the outstanding properties of the final products.

The utility of the colloidal films producible from different fatty oils varies widely and may have little apparent relationship to the original state of unsaturation of the oil. Linseed oil is by far the most suitable vehicle for paints; perilla oil is more unsaturated, but gives a dried film which

is somewhat marred by irregular markings and spots ; China wood (tung) oil is equally unsaturated, but has considerably more tendency to gelatinize or separate in the heterogeneous phase, so that the films produced are frequently dull or matt. Soya bean oil, safflower oil, sunflower seed oil, and other oils of fairly high iodine value and pronounced drying properties do not yield such satisfactory films as linseed oil ; there is a tendency to produce softer, more gummy products. Menhaden oil and, still more markedly, the other fish oils and whale oil, oxidize very readily, but the products tend to be gummy.

These differences can probably be correlated with two fundamental conditions : (a) the types and proportions of unsaturated acids present, and (b) the constitution of the mixed glycerides consequently present in the various oils. Thus, in oils of the soya bean and safflower class there is but little linolenic acid present, but abundance of linoleic acid ; China wood oil contains the conjugated triethenoid elæostearic acid in large proportions ; whilst the fish oils contain only traces of linoleic or linolenic acid, as a rule, with fair quantities of oleic acid and marked amounts of non-conjugated unsaturated acids containing twenty and twenty-two carbon atoms and four, five or six ethylenic linkages. On the other hand, perilla oil contains more linolenic acid than linseed oil and yet does not give so satisfactory a product.

Hence it seems probable that, although the presence of triethenoid combined acids appears to be desirable in an oil in order that it may be a good paint vehicle, some other factor, namely, the composition of the mixed glycerides as such, is equally important. For instance, it is now known that linseed oil contains fairly large amounts of both dilinoleolinolenin and linoleodilinolenin :—



Quite possibly the circumstance that each of these acids forms about 40 per cent. or so of the total linseed oil fatty acids causes the proportions of the mixed glycerides mentioned to be approximately equal, and this particular mixture may be near the optimum for producing the best type of oxidized and polymerized film. Possibly, again, greater proportions of combined linolenic acid might result in a mixture of mixed glycerides (*e.g.* in perilla oil) which, in spite of conceivably more intense "drying" properties, would fail to give so useful a film. In the opposite direction, absence or paucity of linolenic glycerides, although accompanied by much larger proportions of combined linoleic acid than in linseed oil (as in soya bean or safflower oils) appears to involve loss of ease of both oxidation and polymerization in the resulting natural mixture of mixed glycerides. Put in another way, the "even distribution rule" (*cf.* Section I, Chapter V, p. 94), which is known to be closely followed in all the "drying" oils under discussion, has the result that, in linseed oil, nearly all the triglyceride molecules will contain at least one linolenic and at least one linoleic group (whilst, as already mentioned, many of them contain two of the diethenoid and one of the triethenoid acyl radicals, or *vice versa*). A higher proportion of linolenic acid, leading to a definite preponderance of glyceride molecules containing two of the latter groups (dilinoleno-glycerides) would seem to be disadvantageous.

The same considerations probably apply to tung oil which, with about 90 per cent. of elæostearic acid in its mixed acids, contains about 70 per cent. of the simple triglyceride trielæostearin: the undesirable features of the polymerized tung oil film may well be due to this high proportion of the triple conjugated triethenoid glyceride present. Morrell and Davis have shown the composition of tung oil glycerides to be as just stated, and have also demonstrated that oiticica oil, with only about 70 per cent. of licanic (ketoelæostearic) acid, contains but little of the simple glyceride trilicanin; the properties of the polymerized oiticica oil film differ considerably from those of

polymerized tung oil, some of the defects of the latter being absent and fresh ones (*e.g.* undue softness and permeability to moisture) appearing, but it must be remembered that glyceride structure is not the only variable in the two oils, for the presence of the ketonic group in licanic acid introduces a new factor into the constitution of the acyl radicals.

Without any attempt at a complete or exhaustive treatment of this most complicated subject, it is hoped that the contents of this chapter give a fairly balanced summary of current opinions upon the mechanism of the oxidative and polymeric processes operative in the transformation of "drying oils" into solid or colloidal films and products.

CHAPTER II.—THE TECHNICAL PROCESSES EMPLOYED IN PREPARING FATTY OILS FOR USE IN PAINTS AND VARNISHES

ANY oil which is to be employed in paints, varnishes, or enamels should be free from dissolved or suspended mucilage and as pale as possible in colour. The presence of a small amount of free fatty acid, as met with in good crude vegetable oils (1–2 per cent. as oleic acid), is not a serious detriment, although the more neutral the oil the greater is its value as a constituent of paints, etc.

The processes most commonly used in preparing fatty oils for these purposes are briefly indicated below, with special reference to linseed and tung oils, which are the most widely used fatty components of paints and varnishes. The other oils which are also employed are subjected to much the same treatments. Certain of the processes described, especially the thickening or polymerization, and the "blowing" of the oils, also lead to materials which are used in some other industries, such as the manufacture of linoleum or patent leather and in leather-dressing. In this chapter all the processes in common use for thickening or oxidizing "drying" oils will be discussed, whether the products are serviceable in paints or varnishes or for application to the various fibres dealt with later in Section IX.

The preparation of fatty oils for use in paints and varnishes comprises, therefore, (i) a preliminary refining of the crude oil to remove mucilage and colouring matter, and (ii) in many cases a further treatment which may either thicken the oil, partially oxidize it, or incorporate metallic driers so that when applied as a film the oil will oxidize and harden rapidly.

Preliminary Refining of Oils for Use in Paints, Varnishes, etc.—Three methods of procedure are chiefly employed in the case of linseed oil :

(a) The oil may be boiled in tanks with strong brine, a 10 per cent. solution of alumina ferric (crude aluminium sulphate) or a 10 per cent. solution of sulphuric acid and then settled. Mucilage is also coagulated if the oil is rapidly heated to 260° C. and then rapidly cooled, but this is not so convenient to manipulate on a large scale as the foregoing methods. Treatment of the oil with expanded superheated steam at 250° (as in deodorization of an edible oil) has also been recommended as a useful alternative to these processes.

The settled oil may be treated with fuller's earth, which adsorbs any remaining mucilage and also bleaches the oil to some extent. The fullering treatment follows the usual procedure as indicated on pp. 221, 222, and is usually carried out at 80–90° C. From 3 to 5 per cent. of fuller's earth, or less of the activated types (p. 224), is agitated with the settled oil ; the earth should be quite dry and precautions taken in order that the finished oil does not become contaminated with steam or moisture.

Linseed oil thus refined is perfectly clear and from pale to full yellow in colour.

(b) The oil may be alkali-refined with sodium carbonate or caustic soda, as described on pp. 231, 232. For the present purpose it is usual to employ only sufficient alkali to neutralize most of the free acidity, leaving about 0·3–0·5 per cent. of free fatty acid in the oil. The separated soap carries down with it all of the mucilage and a fair amount of colouring matter. The neutralized oil is washed with warm water and then, preferably, treated with fuller's earth.

The alkali process is more costly than either the preceding or following method, but yields a product of superior clarity and colour.

(c) The sulphuric acid refining process may be employed and finds considerable application ; careful manipulation

is required, however, in order to avoid incipient charring of the highly unsaturated fatty oil, with resulting deterioration in colour.

The oil is well agitated in a lead-lined tank and sulphuric acid (20–30 lbs. of acid per ton of oil) is added in a thin stream until withdrawal of a small sample shows that the mucilage, etc., has coagulated in small flakes leaving a pale clear oil. Water is then added in the proportion of about 2 gallons for every gallon of acid used, and the whole settled overnight. The clear oil is washed in a fresh tank with about one-quarter of its volume of boiling water, settled and re-washed once or twice. The oil is finally agitated or "beaten" for some hours by revolving blades which dip only a few inches below the surface of the oil; this brightens the oil by removing the last traces of water.

Some linseed oils refine and bleach excellently by the acid process, but others do not become completely pale, although the mucilaginous matter is satisfactorily removed.

Linseed oils can also be bleached by the action of oxygen, either in sunlight, in the rays from a mercury lamp, by exposure to a high voltage "silent electric discharge" ("voltolization"), or by ozonized air. The bleached oils are almost colourless, but a certain amount of oxygen is inevitably absorbed by the glycerides during the oxidation of the non-fatty colouring matter to colourless derivatives.

Linseed oil which has received one or other of the foregoing treatments may be designated refined, pale, or bleached linseed oil, but in the paint and varnish trades those oils which have not been submitted to a further special process as described below are frequently classed as raw linseed oil, in spite of any preliminary refining of the crude oil.

Preparation of Thickened, Polymerized, or "Stand" Oils.—Three methods may be distinguished:

(a) *Fire-heated*.—This is the old system, which is still used to a large extent. The oil is placed in enamelled iron, copper, or aluminium pans which are heated by the hot flue gases from a coke- or gas-fired furnace in an adjacent but separate building. The pans are efficiently hooded so that

escaping volatile and acrid matter can be conveyed away and passed through a furnace to destroy it. The oil is maintained at 260–280° C. until it has reached the desired consistency ; the process occupies as a rule from one to three days.

(b) *Heating by Oil Circulation*.—A more modern method consists in the Merrill (Kestner) process of heating by oil circulation. The transmission of heat from the furnace to the fatty oil is effected by a specially refined mineral oil or suitable individual organic compound (*e.g.* diphenyl) capable of withstanding the necessary temperature without decomposition. This is circulated continuously through a system of coils, part of which is immersed in the fatty oil (contained in well-lagged pans) and part of which is exposed to the gases from the combustion of air and coal-gas or, preferably, fuel oil. The fatty oil can thus be heated rapidly to 260–280° and kept at a constant temperature, whilst when it is sufficiently thickened it can be rapidly cooled by cutting off the source of heat and substituting a current of cold air whereby the circulating mineral oil is quickly brought to atmospheric temperature.

The colour and quality of the thickened oil is better than when method (a) is employed.

(c) *Top-firing*.—A variant of the open fire-heated form is to heat the oil in an open pan until the escaping vapours ignite freely, the process being continued whilst the top of the oil is covered with a layer of burning vapour. Thickened linseed oil produced in this way is known as “burnt” or “top-fired” oil. The correct manipulation of a top-fired oil in the pan requires considerable skill, but the oil thickens more rapidly and is no more oxidized than a boiled oil if the correct conditions have been maintained. A good top-fired oil is of about the consistency of “thin” stand oil and is the least greasy of any thickened oil ; this creates a demand for burnt oil for certain specific purposes, notably for lithographic inks in copper-plate printing.

It should be carefully noted that the procedure selected for preparing stand oils depends primarily on the oil to be

processed. Most of the above discussion is based on treatments for linseed oil; prolonged heating by whatever process cannot of course be applied to tung oil or other oils containing large proportions of conjugated unsaturated glycerides. Either of the three methods are available, however, for other "drying" oils of the non-conjugated type such as perilla, candlenut, safflower seed, rubber seed, niger seed or sunflower seed oils. In particular, perilla oil appears to be much improved after conversion by "heat bodying" into a thin stand oil.

In the manufacture of tung oil stand oil (and the same applies in a less degree to oiticica oil) care must be taken to avoid carrying the process too far and proceeding to complete gelation. The heat-circulatory system is here almost essential, and in modern practice the tung oil itself is also in continuous circulation so that the time of its exposure to 280° C. or thereabouts does not exceed 2 or 3 minutes, whilst by heat exchangers rapid cooling of the product to below 150° C. is secured. An alternative method is to heat tung oil for a longer time at a much lower temperature (180–200° C.) but this probably leads, on the whole, to a less useful form of stand oil. On the other hand, very useful linseed-tung stand oil mixtures are frequently manufactured, a thin linseed oil stand oil being added to raw tung oil and the mixture then heated at 280° C. until a product of the desired viscosity is obtained.

The chief uses of stand oils (clear thickened oils) are as follows :

As components of nearly all enamels and varnishes (from linseed, or a mixture of linseed and tung oils); for paints which are intended to act as preservatives against corrosion or incrustation by marine organisms (anti-fouling paints); in lithographic varnishes and printers' inks (linseed oils); in the manufacture of plastic masses, in conjunction with fibrous material—artificial flooring, linoleum, etc. (strongly thickened linseed oil); as rubber substitutes and as thickeners for mineral oils (thickened tung and castor oils).

Preparation of Boiled Oils.—Boiled linseed oil is as widely, perhaps more widely, used than raw linseed oil in paints and varnishes; its preparation involves little polymerization or marked oxidation, but consists in heating the oil in order to clarify it and coagulate the last traces of mucilage, whilst at the same time bringing into solution minute amounts of metallic salts (usually lead and manganese, or cobalt resinate or linoleate) and destroying by oxidation and/or heat any natural antioxidant compounds present in the original oils. The metallic salts are then in homogeneous solution in the oil ready to promote its oxidation or drying when exposed on the painted surface.

Formerly the same procedure was adopted as in heating to produce a thickened oil; that is, the oil was heated as rapidly as possible to about 260–290° C. in a fire-heated pan, certain metallic oxides (usually a mixture of red lead or litharge and manganese oxide) were added and the boiling continued for a few hours only until a homogeneous solution was attained.

The modern process is operated at much lower temperatures (130–150° C. being the usual maxima) and “soluble driers” are employed in place of the metallic oxides. The soluble driers consist of the resinates or linoleates of lead and manganese, or of cobalt, which are prepared separately according to various prescriptions, mainly by heating together rosin, linseed oil, and the metallic oxides in determined proportions. The linoleates are better driers and more soluble than the resinates, but the latter are more readily prepared, and in view of the relative cheapness of rosin there is a tendency to use a greater proportion of the latter.

The oils are heated in tanks holding a charge of 10–20 tons and provided with a closed steam coil for heating purposes; agitation and a minor amount of oxidation are secured by the passage of an extremely vigorous current of air in fine streams. The exit air is conducted away to a boiler flue in order to secure combustion of the acrid vapours from the oil. The oil is heated to about 90° C.

and then agitated by the current of compressed air ; the driers (already dissolved in a separate vessel in a little of the oil) are added so that, for example, there is about 0.1 per cent. of lead and 0.03 per cent. of manganese present in the oil, and the temperature is increased to about 120° C. or higher, according to the desired colour of the product (the paler oils are manufactured at the lower temperatures). Agitation with air is continued for about 2 to 3 hours, during which oxidation sets in to some extent in the oil and the temperature may rise above the desired point, in which case cooling water is made to replace the steam in the coils.

The oil is then cooled, pumped into settling tanks and, after standing for some time, is finally filtered through a press ; it should dry completely in the form of paint in from 10 to 24 hours.

Boiled oils, which are termed Extra Pale, Pale-boiled, Double-boiled, etc., according to their colour and viscosity, are employed very largely in paints, varnishes and enamels, and also in waterproofing materials, electrical insulation, patent leather, etc., etc.

Preparation of Blown Oils.—Blown oils are distinguished from boiled oils in that they are oxidized by continued passage of the air current at about 120° C. after any driers present have been brought into solution, and until the desired consistency and degree of oxidation have been reached.

The object of using blown linseed oil in paints, varnishes, and enamels is mainly to replace the stand oils or polymerized oils, which are somewhat more expensive to manufacture, but are also in general of better quality. Blown linseed oil, however, wets certain pigments better than raw or boiled oil and also causes varnishes to flow better ; it is therefore used in the preparation of some paints in admixture with a large proportion of raw oil (chiefly for heavy pigments of the type of white lead or ochres) and in varnishes. The fatty components of some of the cheaper varnishes are blown linseed oil mixed with some China wood (tung) oil.

By prolonged blowing linseed oil is converted into a plastic mass which is an essential component of linoleum and similar materials, whilst other oils are blown before being applied in other industries. It is convenient to deal with all the methods of production of blown oils in one place, and therefore the outline now to be given covers the production of blown oils in general and not only those destined for use in paints and varnishes.

Blown Oil for Paints and Varnishes—The operation is carried out in a similar plant to that used in the modern process for boiled linseed oil. The linseed oil is heated to about 60° C., when a very small amount of drier (preferably a soluble cobalt drier) is added and the blowing commenced. The temperature should not be allowed to rise much above 120° C. in order to obtain a pale oil of reasonably low acid value; formation of free acids to a greater or less degree is inevitable during the progress of the oxidation above 100° C. The oil must be cooled to below 70° C. before racking off in order to avoid darkening in colour.

The process may occupy from about 6 to 20 hours, according to the adaptability to oxidation of the raw oil and the extent to which its specific gravity (which is a measure of its consistency) is to be increased.

Blown Linseed Oil for Linoleum, etc.—This is manufactured by three methods, namely, two devised by Walton in 1860 and 1894, and one by Taylor and Parnacott in 1871.

Walton's 1894 process is now conducted on the lines of that described above for blown oil for paints, but the operation is commenced at 50° C. by allowing linseed oil containing metallic driers to fall through the perforated base of a trough through air into a lower tank, where it is pumped back to the upper trough and re-percolated through air until it becomes too thick to pass the perforations easily. It is then transferred to a steam-jacketed agitator known as a "smacker," and violently agitated with a strong current of air at about 55° C. until it becomes crumbly, after which it is stoved in trays at 40° C. for two or three days, cooled

and shredded by machinery. This method became known as the "shower-bath and smacker" process.

The Taylor-Parnacott method is operated at about 150°C . and finally 260°C . in vessels similar to those employed in manufacturing stand oil (p. 477), but with the addition of a continuous current of air during the operation. Polymerization and oxidation therefore proceed concurrently, and the conversion into linoleum or rather "corticine" material is attained more rapidly than in the Walton process. The product, however, is much darker in colour and more tacky, and is not very suitable for linoleum; when heated and mixed intimately with cork, coarse sawdust, or wood fibre it yields useful materials formerly known as "corticine" and now more generally termed cork mats or carpets.

Finally, Walton's first process of 1860, known as the "scrim" process, is now falling into disuse. It consisted in causing linseed oil (containing a lead dryer) to flow downwards over a mass of loose cotton fabric (termed "scrim") which is suspended from the roof of a fairly lofty chamber (about 24 feet high), the latter being maintained at $35\text{--}40^{\circ}\text{C}$. Some of the oil dries on the fabric and the rest flows on to the floor, where it is drained and pumped back again to the roof and sent over the fabric. In the course of two or three weeks the fabric becomes coated to a depth of about half an inch or more with solidified linseed oil. The oxidized oil layers are peeled off and roughly shredded through rolls.

The "short," crumbly products produced in shred-form by either of the Walton processes are next mixed with about one-third their weight of resin and kauri gum in a steam-heated agitator. Heat and stirring are applied until the mixture becomes pasty and coalesces, after which it is run on to moulded floors to set, and is then technically known as "cement."

Other Blown Oils.—Certain other oils are blown to a greater or less degree by the process already described for blown oils for paints, the products finding various technical applications.

Thus menhaden oil is blown to a large extent in the United States, where it is mainly used in the production of linoleum; it also replaces blown linseed oil to some degree, but not altogether satisfactorily, in the American paint industry.

Rape oil and cottonseed oil are blown in order that the products may be mixed with mineral oils to produce specific lubricants. Oxidized fatty oils are in general completely miscible with hydrocarbon oils and serve to increase the viscosity of the latter; for many purposes, where the presence of oxidized oils is not objectionable, this procedure represents a convenient and economical method of securing a cheap lubricant of high viscosity.

Whale oil and fish oils are also blown for the same purpose and for use in certain phases of the tanning and leather-dressing trades.

In all these cases the procedure adopted at the present time is that of blowing with air in steam-heated pans, usually in presence of traces of cobalt driers, at a temperature not exceeding 120° C.

CHAPTER III.—FATTY OILS AND WAXES EMPLOYED IN PAINTS, ENAMELS, VARNISHES, AND POLISHES.

THE coverings mentioned in the title of this chapter can be grouped in three divisions :

(i) **Paints and Enamels.**—These consist of mixtures of colouring matter (usually of a mineral or inorganic nature) with fatty oils and other organic compounds, the object being to secure the covering of a solid surface with an even adherent coating of white or coloured pigment, with or without a glossy finish.

(ii) **Varnishes.**—These are designed to produce a rich, highly glazed finish, and consist essentially of one or more gum-resins dissolved in a mixture of drying oil with a “thinner” (usually oil of turpentine). Some colouring matter may also be present, but the colour function is subordinate to that of producing a rich, smooth, glossy surface.

(iii) **Polishes.**—These, of course, are not adherent to the solid surfaces in the same sense as paint, but are applied by mechanical rubbing. A non-volatile oil is therefore undesirable, and the place of the drying oil film is taken by a wax which is left as an attenuated film on the solid surface after application of the polish.

Paints.—Ordinary paints are prepared by grinding together a fatty oil and the mineral pigment or mixture of pigments, which must be in a very fine state of subdivision (below 100 or 200 mesh). In this way a more or less homogeneous dispersion of the solid particles in the liquid oil is obtained, but the paints as made up usually contain only sufficient oil to bring the solid into complete suspension, and contain as much as 60–90 per cent. of solid pigment (according to the nature of the latter). Further

oil is added by the painter to produce a paste of consistency which will flow correctly under the brush, and frequently non-fatty thinners (usually oil of turpentine) are also added for the same purpose. The thinners are volatile and evaporate away, leaving the fatty oil to "dry" and harden by the process of superficial oxidation.

Linseed oil is the staple fatty oil of the paint industry, and is used either in the raw (or refined) or the boiled state, according to the predilection of the painter. Most frequently a mixture of raw and boiled linseed oil is preferred, although the use of boiled oils alone appears to be increasing.

In spite of the predominance of linseed oil as a paint vehicle, attempts are continually being made to utilize other drying oils, especially in America and Asia. This is perhaps due to the somewhat erratic variations in the flax crop, which have resulted from time to time in the price of linseed oil becoming relatively high.

No single oil has yet been found which is accepted as equal to linseed oil for use in paints, but it appears quite likely that some oriental and tropical seed oils, if cultivated in as carefully selected strains as the flax, would rival linseed oil. For example, perilla oil from the East Indies and Japan dries excellently, and defects observed when the oil is applied raw are much reduced when the partially polymerized (heat-bodied) oil is employed; at present it is somewhat of a rarity, but its cost of production and utility might both be changed advantageously if its cultivation were systematically undertaken. The same argument applies to lumbang or candlenut oil, and certainly to China wood or tung oil, all of which are derived from different Asiatic or American species of *Aleurites*. Lumbang or candlenut oils are possible substitutes for linseed oil in paints, tung oil is more suitable in place of linseed oil in varnishes (*cf.* below), although it can be mixed usefully with the latter for use in paints, especially if previously heat-treated. Hemp seed oil is largely used on the Continent in paints and varnishes.

Other vegetable drying oils, notably soya bean, rubber-seed, and safflower oils, are of little use alone, either drying too slowly or leaving a soft and tacky product. The fish oils, also, although rapid driers, yield soft and gummy products. In many cases, however, these oils can be usefully blended with linseed oil (in the proportion of 25 or even 40–50 per cent. of added oil); in this way, soya bean oil, safflower oil, menhaden oil, and Jap fish or Japanese sardine oil have been used in conjunction with linseed oil with favourable results.

When employed as paint vehicles, the oils other than linseed oil are in general first of all boiled with a suitable drier, and the most useful metallic driers (both as regards basic and acidic components of the salts) vary from one oil to another. The literature on the suitability of particular driers for given oils is consequently voluminous, and must be consulted in detail where further specific information on these points is required.

Artists' Paints.—For artists' oil colours it is necessary to use fatty vehicles which remain perfectly colourless after drying. The best linseed oil gives a film which is almost colourless, but which develops a slight but perceptible tinge on ageing. Walnut oil and poppy seed oil, however, remain perfectly colourless, and also, although they yield a hard permanent lustrous film, dry much more slowly and evenly than linseed oil: this is obviously as great an advantage in artists' paintings, as the relative slowness is disadvantageous to the ordinary painter. Of course, the oils must be colourless from the commencement, and walnut or poppy seed oil for artists' paints is obtained only from the first cold pressings of the seeds and is, if necessary, subjected to bleaching by sunlight before use; consequently the price of these oils is much greater than that of linseed oil. These two oils have, however, been the favourite medium of artists since their employment by the great mediæval and Renaissance painters—although their use in paints, like that of linseed oil, dates from still earlier periods.

Enamel Paints.—An enamel paint is a mixture of solid pigment with a gum varnish, so that the final effect is a combination of even colour with the very high gloss and rich finish characteristic of a varnished surface. So far as the fatty components are concerned, enamel paints are to be classed with the varnishes, some description of which follows. It is clear that, as regards permanence and protective action against atmospheric effects, an enamelled surface is equal to that of a varnished surface, and superior to one coated with paint alone.

Varnishes.—It has been already indicated that the function of varnishes is primarily that of producing a rich glossy surface, the thickness and body of the varnish film also acting as a better protective covering than paint alone.

The fatty oil varnishes, with which we are here concerned, consist essentially of a stable solution of certain natural or artificial resins in a fatty oil. Resinous materials, if suitably hard, can usually also be applied in a film when dissolved in volatile solvents, for example, the lower alcohols or their esters, acetone and some other ketones, or hydrocarbons such as oil of turpentine (pinene) or tetralin (tetrahydronaphthalene). Varnishing materials of this type, into which fatty oils do not enter, are known as spirit varnishes or lacquers and can only be considered in this work in regard to their competitive aspect with reference to the fixed oil varnishes.

The components of fixed oil varnishes are of three essential types : gum resins, fatty oils, and volatile thinners.

The Resin Components of Varnishes.—The old-fashioned varnishes, which are still in great favour with decorators, contain one or a mixture of certain fossil resins, notably copal, dammar, gum-zanzibar, shellac, or similar materials. The fossil resins, which have become thoroughly hard and stable through age-long exposure, give the best results ; they are, however, not miscible with fatty oils until after a preliminary heat or solubilization treatment. Exactly what takes place during this process is still unknown ; a certain amount of "cracking" or depolymerization

undoubtedly sets in, and possibly also some combination of the resin acids with glycerine from the fatty oil which is added during the operation.

The copal or other resin is heated at about 300° C. for some hours, until it "runs" suitably, after which it is cooled somewhat and about 25–30 per cent. of its weight of boiled oil is cautiously added and the whole heated up again as before for about an hour. The product is then soluble in boiled oil. The process demands great skill in manipulation in order to minimize losses and conserve the quality of the varnish; under the best conditions about 25 per cent. of the resin may be lost in the form of volatile products of decomposition.

In order to lessen the losses due to destructive decomposition, it has been proposed to heat the resin in solution in naphthalene or phenol, or with about 20–30 per cent. of ordinary rosin, under a pressure of several atmospheres at 280–300° C. Alternatively, a mixture of gum-resin and rosin may be thus treated, after which glycerine is added and the mixture again heated at 280° C. without pressure in order to esterify the gum-resin acids. In this way copal or other resin esters are produced, and these are somewhat largely used at present in varnishes.

Ordinary rosin (*cf.* p. 379), obtained in large quantities as a residue in the manufacture of turpentine oil, is too soft and tacky to be of direct use in a good varnish, but it can be improved by either of the following processes :

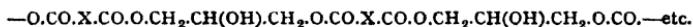
(i) The rosin is heated with good stirring in a copper or an aluminium still and, when quite fluid, about 10 per cent. of its weight of glycerine is added, and the temperature raised to 280° C. whilst the pressure is reduced to about 100 mm. The rosin acids are partially esterified by the glycerol, and the resulting rosin ester is a neutral product of considerable hardness which can be used in varnishes.

(ii) If rosin is heated at about 260° C. with 6–10 per cent. of pure lime and the correct amount of boiled oil, calcium rosinate (abietate) is produced, and this dries to a glossy film on application to a surface. If colour is not important,

other metals such as iron or manganese may be introduced in place of calcium. The metallic rosinates have much the same properties as regards hardness and texture in a varnish as the natural fossil resins, but are not so permanent and, especially in the case of calcium rosinates, are apt to develop a spotted appearance with age.

Finally, a few of the modern soluble synthetic resins are used with fatty oils, although for the most part they are employed in the form of lacquers with volatile solvents. In place of copal resins, cumarone and indene resins, manufactured by polymerization of the solvent naphtha fraction, b.p. 160–180°, from coal tar with small quantities of sulphuric acid, may be used with linseed and/or tung oil stand oils in varnishes; these polymers range from pale to deeply coloured, and from soft to hard resins, and the paler hard varieties are of course the most suitable for varnishes.

The most important development in synthetic resins for varnishes into which components of fatty oils enter is connected with the glyptal or alkyd resins. This group consists of complex esters of organic dicarboxylic acids with polyhydric alcohols (or their monoalkyl ethers), formed by heating together the acid anhydride and the polyhydric alcohol; the polymeric nature of the products results, of course, from union of the dicarboxylic acid molecules each with two different molecules of the alcohol:



The most common forms of this class are the complex glycerol-phthalic acid esters produced from glycerol and phthalic anhydride, which, as such, have valuable properties as plastics. For varnishes, however, they are somewhat too hard, or, at all events, their usefulness is improved if they are softened or made more resilient by the incorporation of a "plasticizing" or softening component. For the particular purpose in view, this may be effected, and at the same time the resin itself may be given "drying" properties, if some of the free

alcoholic groups left unesterified by the phthalic anhydride are united with "drying" oil acids. Thus the glyptal resin may be esterified with linseed oil fatty acids, or heated at about 280–300° with linseed oil itself, when a substantial amount of "ester-interchange" takes place between the components. Linseed oil or its acids are the best for this purpose, although other oils rich in linoleic acid (but preferably also containing some linolenic acid) may be used in place of it.

The Fatty Oil Components of Varnishes.—Boiled linseed oil was formerly the most favoured fatty constituent in copal varnishes, but linseed oil stand oils have been increasingly used in its place for many years past, the extent of the heat-bodying or heat-thickening depending upon the type of varnish to be produced. For linseed oil varnishes, therefore, it may be said that the fatty component consists of linseed oil stand oils, sometimes in admixture with boiled linseed oil. It is possible, but not so easily or satisfactorily as in the case of paints, to replace these linseed oils by corresponding products from other "drying" oils of the non-conjugated di- (and tri-) ethenoid type, but the choice is restricted by the unsuitability of slow-drying oils and of those which give softer films, such as soya bean, safflower seed and the fish oils. On the other hand, heat-bodied perilla or candlenut (*lumbang*) oils are quite useful as varnish media.

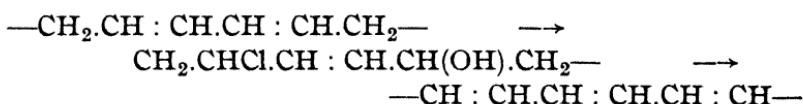
Of late years, especially with the expansion of the still not too certain supplies of Chinese (and latterly, American plantation) tung oil, the latter has tended to supplant linseed oil as the first favourite for varnish oils. It has already been mentioned that the use of the raw oil has certain disadvantages, but that these largely disappear after its conversion by heat treatment into a tung oil stand oil. Still better results are frequently experienced by the employment of stand oils prepared from mixtures of tung and linseed oils, and these are probably the best type of varnish oils now in use. Doubtless, some inter-esterification (interchange of acyl radicals) takes place between the linseed

oil and the tung oil glycerides during the heat-bodying ; it is possible to achieve this more definitely by first heating tung oil with glycerol so that a certain proportion of diglycerides and monoglycerides are produced, after which the product is reconverted to a new mixture of mixed triglycerides by esterification with linseed oil fatty acids. A similar effect may be obtained more cheaply by heating tung oil with rosin, rosin esters or calcium " rosinates," or by re-esterifying the product of heat on tung oil and glycerol with rosin acids (instead of linseed oil acids as above). The use of rosined oils in the better class of varnishes is, however, detrimental and these products are found mainly in the cheaper varieties.

The growing preference for tung oil in varnishes, and its occasional scarcity, have led to enquiries for other " drying " oils with a high content of unsaturation. Other oils rich in elæostearin are at present rarer than tung oil itself, but a certain quantity of oiticica oil, rich in ketoelæostearic glycerides, is available from time to time. This oil, however, yields a film which, although in some ways resembling that from tung oil, is more permeable to moisture and is also of a somewhat softer type.

Attempts have also been directed for some years past to the transformation of non-conjugated unsaturated oils into others containing a conjugated di- or tri-ethenoid system. Scheiber proposed to add hydrogen chloride or hypochlorous acid to the unsaturated acids of such oils as linseed or poppy seed and to remove the elements of hydrogen chloride (and water) so as to produce conjugated unsaturated glycerides containing one more ethenoid bond than the original material, but at the time of writing this does not seem to have developed into a large-scale process. Scheiber also described a product " Synourinol " obtained by the dehydration of castor oil or its acids and consisting largely of the conjugated $\Delta^9,11$ -octadecadienoic acid ; other workers have reported on the dehydration of ricinoleic glycerides or acids to diethenoid compounds (which takes place fairly readily) but there exists at present considerable difference

of opinion as to the proportion of the conjugated form present in the product, and some communications place this as low as 30 per cent. of the diethenoid acids, the remainder being Δ^9, Δ^{12} -octadecadienoic compounds. Blom has described the conversion of the diethenoid product from castor oil into a conjugated triethenoid fat by adding hypochlorous acid to the former and subsequently removing hydrogen chloride and water from the product :



The above are at present more in the nature of suggested processes than of methods which have been brought to commercial production, but the activity evident in this field leads to the conclusion that a technical conjugated triethenoid oil derived either from castor oil or from oils of the "drying" or "semi-drying" groups is a likely achievement of the near future.

The actual proportions of fatty oils employed, and the relative amounts of stand and boiled oils, depend upon the particular type of varnish ; innumerable recipes exist, the details of which cannot be entered into here.

Volatile Thinners.—In order to assist the flow of varnish during application, it is thinned with a suitable oil of medium volatility at the ordinary temperature, the best material being oil of turpentine. The turpentine is not only a volatile solvent, but is capable itself of fixing atmospheric oxygen in what is probably a labile peroxidic form, and this may well accelerate the drying of the boiled oil present.

In the cheaper varnishes the best oil of turpentine is replaced by cruder qualities known as wood or knot oil, obtained by destructive distillation of the waste wood and roots of pines, instead of from the colophony or exuded resin. Hydrogenated naphthalene (tetralin) has also found application as a varnish thinner, especially in Central Europe. Tetralin boils at $206^\circ \text{C}.$, is moderately volatile

at atmospheric temperature, and is stated to replace turpentine quite adequately.

Polishes.—The use of natural waxes in polishes for wood, linoleum, leather, and other materials can only be discussed from a general standpoint, since they include a wide variety of specific mixtures ranging from high-class materials down to almost any mixture which is capable of imparting some sort of smoothness and shine to the surface treated.

Solid polishes of the better qualities depend for their main components on natural waxes (notably beeswax) mixed with good oil of turpentine, while semi-liquid polishing pastes or creams may consist of an emulsion of wax and potassium carbonate solution with oil of turpentine prepared at a moderate temperature. The free fatty acid always present in a natural wax yields a certain amount of potash soap which acts as an emulsifier for the neutral wax esters and the turpentine.

Beeswax is the chief fatty component of the best polishes, but the greater part of the ordinary wax polishes on the market contain little or none of this material.

Carnauba wax is a good and frequent substitute for beeswax, but the basis of many modern polishes is paraffin wax or a mixture of this with hard stearine (stearic acid). Thus the composition of the "wax" is frequently similar to that of a modern candle, except that in order to produce a sufficient degree of hardness a certain amount of carnauba, candelilla, or montan wax is added to the mixture.

The compounding of polishes has remained largely empirical, and the technology of waxes has not been developed in the systematic manner which is more or less characteristic of the fat industries. Compared with the latter, the amount of wax involved is of a small order: numerous waxy materials, whether true waxes, hard fats (Japan wax or stearins) or petroleum products, are at hand in addition to the somewhat expensive beeswax; the effect to be produced is of a superficial and temporary nature, and no very precise standards of efficiency are demanded. In consequence of all these factors the technology of wax

polishes continues to be relatively simple and of the "rule of thumb" type. It should be noted, however, that the natural resources available in waxes have been by no means thoroughly explored, and it is probable that more important uses for this class of the fats than as polishing materials, components of gramophone records, etc., or of salves and ointments, or as illuminants, remain to be discovered in due course.

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SECTION IX.—THE APPLICATION OF FATS TO FIBRES

Introductory.—The uses of fatty materials which are dealt with in this section are those in which the fats are combined, in one or other way, with various natural fibres. Whilst, ultimately, the fat is in nearly all cases combined as a more or less external film or layer on the actual threads or fundamental components of the textile material, these applications are mainly distinguished from those dealt with in the preceding section in that the fat penetrates into and through the whole of the bulk of the material, instead of forming a purely external coating or varnish.

The range of materials to be included in this group is somewhat diverse, and the discussion of the technique involved is consequently more discursive than in most of the preceding sections.

We shall consider first of all the case of linoleum and of other oiled fabrics : these are in some degree intermediate between varnishes and the application of fats to textiles or leather, since they all consist of a more or less thick layer of highly oxidized oil (with gums or resin) which is mounted on a textile backing or canvas, either of jute, cotton, or other textile fabric.

The use of fats in the cotton industry is quite specific and different in type from the others, because the "Turkey red oil" or other "textile assistant" used acts not only as an improvement to the fibre, but also as a fixative or mordant for many of the dyes used in cotton printing. Most of the fatty compounds used with cotton fabrics are therefore detergents or wetting agents belonging to the group discussed in Section V., Chapter VII. (p. 396).

In the woollen-weaving trades specific types of fatty oil are used as lubricants during the spinning operations, and in this case care has to be taken to select fats which are not of a "drying" or even "semi-drying" nature.

Finally, in the production and tanning of leather and also in the manufacture of patent leather, fatty oils of various kinds are used at various stages, and a brief account is given of the chief oils which are in general use in these trades.

CHAPTER I.—THE PRODUCTION OF LINOLEUM; WATER-PROOFING AND INSULATING FABRICS

VERY large quantities of linseed oil and a few other drying oils are employed in the production of floorcloth or oilcloth, linoleum, corticine or cork lino, and for oiled fabrics intended to resist penetration by moisture or to be non-conductors of electricity. For many of these purposes the oil is first of all prepared or blown as described in Section VIII., Chapter II., and in other cases the oxidation of the oil, as in the case of varnishes, takes place after it has been applied to the fabric. Some of the more extensive applications of drying oils in this way will now be considered.

Oilcloth or Floorcloth.—This material is now falling into disuse in consequence of the cheapened production of the more durable, more artistic, and more hygienic linoleum, but it is still produced on a considerable scale. Two main methods of production are practised, the hand and machine processes, the latter being in more common use.

Oilcloth consists of a woven canvas (jute) backing, coated on both sides with several layers of oil-paint. Linseed oil is the best and most widely used oil for the purpose, but in America menhaden oil is also largely employed, whilst hemp seed, soya bean, and sunflower seed oils, amongst others, have been used from time to time in the manufacture of both oilcloth and linoleum.

In the older manual process, the woven canvas is suspended in 25-yard lengths on frames 8 yards in height. It first receives a coating of size, and then three coats of paint, on each face : to the back of the canvas red (iron oxide) or yellow (ochre) paint is applied, whilst that on the face is white or at most pale-coloured. Each coat is left for about

ten days to dry, and before the second and third coats are applied the face of the canvas is smoothed by the application of a "knotting-knife," followed by rubbing with pumice stone. The paint is applied by means of a trowel, and two further coats (making five in all) are applied to the face, the last being brushed on. After further drying the painted cloth is rolled up and taken to the printing machines to receive a coloured pattern on the face or upper side.

In the machine process a roll of canvas about 400 yards long is first passed through a sizing machine, thence over a number of steam-heated rotating drums to the paint-coating machine. This consists of two iron rollers, around which runs an endless rubber apron, which supports the canvas whilst paint is laid and spread upon it by a steel knife, which also scrapes off any unevenness of paint or canvas surface ; the canvas passes from the rubber apron into a heated stove and back to the apron for a further coat of paint, until it has received two coats on the back and four on the face. After passage through revolving pumice-stone rollers to smooth the surfaces the cloth is ready for printing.

The printing of oilcloth is carried out in machines very similar in construction to those used in the calico-printing industry, with the exception that in general the pattern is raised on the wooden surface of rollers consisting of a steel core, instead of being engraved on copper rollers.

"American" Cloth, Table Baize, etc.—The waterproof coverings of thin canvas which are extensively used as rough covers for tables, benches, counters, etc., consist of a sized woven fabric of finer texture than oilcloth canvas, usually left unpainted on the reverse, but covered on the upper surface with about three coats of a good boiled oil paint which produces a glossy surface of any desired tint, impermeable to water and readily cleansed by washing.

Linoleums.—Ordinary linoleum is made from fine cork dust and oxidized fatty oil "cement" prepared as described on pp. 482, 483. The fine cork dust, with or without wood meal, and a suitable proportion of oxidized oil and resin "cement" are ground together in a series of horizontal

mixers or kneaders with the result that a dough-like mass is formed. This passes through a calender, or machine comprising four heavy steam-heated rolls, over which a canvas backing travels ; the dough is delivered on to the canvas and pressed firmly into its surface in the first pair of rolls, whilst the function of the second is mainly to smooth and polish the face of the material. After leaving the calender the linoleum roll is cooled and passed through a backing machine, in which the reverse side is coated with a layer of oil paint. It is then stoved for two or three weeks and is ready for use (plain linoleum) or for transference to the printing machine. Good average household linoleum weighs about 5-6 lbs. per sq. yard and is about 2-3 mm. thick, but high quality linoleum may be up to 8 mm. in thickness.

Inlaid Linoleum.—Whilst the wearing qualities of plain linoleum are satisfactory, the pattern on the printed varieties is bound to suffer with wear, and this has led to the production of inlaid linoleum. This consists of a mosaic pattern made up of segments of coloured linoleum cement, which are prepared first of all and then bound on to the canvas backing by heat and pressure. The pattern is thus carried through to the canvas and is not merely a superficial coating.

Leake's process for producing inlaid linoleum employs stencil plates for each colour, the powdered cement being fed through the stencils on to the canvas and pressed into it by passage through heated rolls or hydraulic presses, followed by calendering to produce a polished surface. Walton's more rapid process consists of first preparing sheets of linoleum cement of the requisite tints and thickness and, by means of a highly complicated machine, cutting out from these the pieces required and assembling them to make up the pattern on the canvas backing, where they are consolidated to produce a homogeneous and accurately fitted material by heat and pressure. The modern machine for this purpose is continuous and practically self-operating, and may deal with as many as ninety million separate units of the cement pattern per day.

Corticine or Cork Linoleum.—Whilst ordinary linoleum is also made from powdered cork, the name cork linoleum, or formerly corticine, refers more particularly to materials made by the Taylor-Parnacott processes (*cf.* p. 483). The cement is produced by blowing linseed oil at a higher temperature than in the Walton processes, and is darker in colour and somewhat less hard in texture. Amalgamation of the cement with granulated cork, wood meal, and resin is carried out practically as in the manufacture of ordinary linoleum (*v. supra*), but the cork is employed in a much coarser state—usually between 20 and 60 mesh. The product may be pressed on to a canvas backing or made up in thicker slabs without any canvas ; in the latter form it is largely used, for example, as bath mats, etc. In either case, owing to the coarser fragments of cork which have been employed, the surface of the material is rougher and less close than ordinary linoleum. This, and the larger proportion of cork present, cause corticine to be a poorer conductor of heat than ordinary linoleum, and consequently it is warmer to the feel ; furthermore, it is more silent when walked upon, and is therefore useful in institutions where absence of sound is desired.

Wall Coverings.—The “Lincrusta” and similar types of embossed coverings for walls and ceilings are practically a form of linoleum, and are manufactured on very similar lines by processes which make use of similar general technique.

Waterproof Fabrics.—Although in recent years cellulose ester dopes and also synthetic resins have come to the forefront as waterproof coatings for various kinds of textile fabrics, most oiled fabrics prepared so as to resist the action of atmospheric moisture were formerly, and are still to a large extent, composed of material impregnated or thoroughly painted with boiled linseed oil. For example, as a matter of historic interest, the oiled silk of balloons was made by thorough impregnation and painting with best quality boiled oil. Many other types of waterproofing material also contain oxidized fatty oil films as essential components ;

the most familiar example is probably tarpaulin, which consists of coarse canvas impregnated with a mixture of a number of substances impervious to moisture, stearine pitch from the residues of fatty acid distillation (p. 280) being a common ingredient, whilst the whole is applied in solution in, or covered with several coats of, boiled linseed or other fatty oil.

Innumerable variants of the fundamental general method of proofing with fatty drying oils and other fatty or wax components are disclosed in the patent literature, but it does not appear necessary here to do more than indicate the general lines on which fatty materials have been utilized for this purpose ; at the same time it should be remembered that the same end is attained in many cases by the employment of quite diverse products, including resins, natural or synthetic, cellulose derivatives, inorganic salts, and many other classes of chemical compound.

Electrical Insulating Materials.—The insulation employed for electrical wiring, coils, transformers, etc., varies according to the voltage concerned, but for many purposes a thin closely woven fabric which has been thoroughly dried and then impregnated with what is essentially an oil varnish is found to be very suitable.

Varnishes for impregnating windings, insulating paper or fabric, fibres and tapes are made from boiled linseed oil incorporated with shellac or resin or asphaltum and thinned with turpentine. Tung oil is sometimes blended with the linseed oil. The required characteristics for a good insulator are high dielectric capacity, flexibility, permanence, resistance to the action of hot oil, and, above all, impermeability to moisture. Two most important points in the technique are, therefore, the complete removal of all moisture from the fabric which is to be impregnated, and complete oxidation or drying of the impregnated fatty oil, since the presence of some unoxidized oil will lead to a certain absorptive capacity for moisture, followed by swelling and deterioration of the varnish film.

In the most recent plants for impregnating fabrics

(usually cambric or paper) with oil varnish, the drying of the fabric, impregnation with varnish, and oxidation of the latter are carried out consecutively in the same vessel. This vessel consists of a closed pan jacketed externally with dry steam coils, fitted with a vacuum pressure gauge and safety-valve, and connected to both a vacuum pump and an air-compressor; it is also in communication with a second vessel, an agitator fitted with closed steam coils in which the varnish is mixed, thinned, and heated to a suitable consistency for impregnation.

The fabric, which is as closely woven and even in texture as possible, is placed in the first vessel or vacuum impregnator and placed under reduced pressure and moderate heat, in order to render it completely anhydrous. Communication is then established with the varnish tank by means of a valve, and the liquid varnish flows into the evacuated impregnator and covers the fabric; after a suitable period the unabsorbed varnish is allowed to drain away as completely as possible. The impregnator is then filled with compressed air to a pressure of 50 lbs. per square inch, and heating continued; by this means the varnish is pressed thoroughly into the fabric and at the same time it is oxidized. To complete the latter process the finished product may be placed in stoving ovens and submitted to the action of a steady current of hot air for several hours.

An oxidized linseed or tung oil film has very high insulating power, but as usual it must be added that substitutes exist which closely approximate in insulating properties to those of linoxyn; these are applied in solution in a more or less volatile solvent, and here the oxidizing process is avoidable. Consequently, the same end can be achieved in the same plant by a process of simple impregnation and evaporation. At the same time, the flexibility, wearing power, and dielectric strength of the oil-varnished insulating fabrics cause them to retain considerable favour with electrical engineers.

CHAPTER II.—THE “WOOL OILS” OR “CLOTH OILS”

SPINNERS and weavers of cotton, wool, flax, silk, and rayon fibres employ large quantities of oil as lubricants for the moving parts of the looms. These light spindle oils are nowadays almost entirely derived from suitable petroleum fractions, which have taken the place of any fatty oils such as neat's-foot oil which may formerly have been used. Except for any “blending” of small proportions of certain fatty oils or their acids into these lubricants (*cf.* Chapter III., p. 516), the use of fats in the textile industry is almost wholly confined to one class, namely, wool fibres. Here the fatty oils are required as a lubricant or softener for the wool fibres themselves because, in consequence of removal of the natural fatty matter by scouring, the fibres or “tops” are rendered comparatively brittle. Treatment with a suitable oil is required in order to facilitate the passage of the yarn through the looms and to reduce its liability to snap during the spinning and weaving processes.

It will be remembered that the raw wool itself contains a definite proportion of fatty material with which, however, co-exist considerable quantities of cholesterol and iso-cholesterol esters and also the free alcohols. This wool fat or wool grease, whilst otherwise objectionable, also has not the necessary lubricating properties and is removed more or less completely prior to the spinning and weaving processes.

The scoured wool is moistened with the wool or cloth oils before passing on to the machines, and the oiled material presents a certain amount of difficulty owing to its liability to spontaneous combustion unless the type of oil used is carefully controlled. Oils of a readily oxidizable nature,

spread out in a thin film over the surface of the oiled fibres, are obviously in an ideal condition to absorb atmospheric oxygen with resultant development of heat. The heat generated cannot as a rule be dissipated very rapidly, and consequently the fibre becomes heated up until the entire mass may commence to smoulder and finally burst into flame.

It is therefore very necessary to determine the liability of the oils used to undergo spontaneous oxidation and development of heat, and an important indication of the suitability of a wool or cloth oil is furnished by an apparatus known as a "cloth oil tester." Various forms of apparatus, such as the Mackey or the Ordway types, are used for this purpose, that of Mackey consisting of a wire-gauze cylinder placed centrally in a jacketed metal vessel fitted with a lid. The lid contains a central hole through which a thermometer, fixed by a cork or cap, passes into the centre of the wire-gauze cylinder, and also an open inlet tube reaching nearly to the bottom of the vessel and an exit tube flush with the top of the lid; air is circulated at a constant slow rate of flow through the inlet and out at the exit. Seven grams of standard cotton-wool are thoroughly and carefully impregnated with fourteen grams of the oil under test in a basin, and the soaked cotton-wool is then packed loosely round the bulb of the thermometer inside the gauze-cylinder. The latter is then placed in the jacketed vessel, the lid secured in position, and the vessel heated to 100° C. by means of boiling water in the jacket, whilst air is slowly circulated as stated. The temperature shown on the thermometer should not exceed 100° C. after one hour's heating, any inclination to rise above this point being an indication that the oil treated is unsuitable for use as a wool oil. Further information can be gathered by continuing the test until the thermometer reaches 200° C. or higher, the maximum temperature reached being considered in relation to the time taken for its development, *i.e.* the slope of the temperature increase/time curve being used as a further basis of comparison.

Kaufmann and Fiedler hold that the latter measurements, taken in conjunction with the difference between the iodine and thiocyanogen values, give good indications of the suitability of fatty oils or oleines as wool oils. Garner has advised additional tests to supplement the Mackey oil tester, namely, the "peroxide accumulation rate" and suitable "cloth ageing tests." The former involves not merely the initial peroxide value (*cf.* Section IV., Chapter VII., p. 327) of the oil but the rate at which peroxides are produced during its exposure to atmospheric oxygen, whilst the latter depends on discolouration of white woollen fabrics after treatment with the oil and subsequently digesting under standardized conditions with alkali.

Since even semi-drying oils such as cottonseed oil do not pass the above tests satisfactorily (whilst linseed oil or fish oils are still less admissible), their employment as cloth oils is most undesirable. It should further be noted that such an oil, stabilized by addition of an antioxidant material (a useful technique in delaying the onset of ordinary oxidative rancidity), is even more dangerous than without such addition, for in due course the antioxidant will be destroyed and heat of oxidation will then develop as much as ever. The use of antioxygenic stabilizers in the case of cloth oils is thus an added source of potential danger, and not a safeguard.

Olive oil has long been the most acceptable material for oiling wool, whilst other "non-drying" oils, including neat's-foot or lard oils, have also found employment, together with distilled oleines of good quality. The comparative expense of olive oil, and certain possible disadvantages in the use of the free acids (oleines) have been partly overcome in recent years by the introduction of several substitutes. For instance, some considerable quantity of olive oil acids (recovered from low grade olive oils and distilled) are now esterified with glycerol and sold as "reprocessed olive oil" for wool oils; these are equivalent for the purpose to a good quality olive oil, providing that the content of linoleic acid in the esterified acids is suitably

low (5 per cent. or less of the total fatty acids). Other products are derived from groundnut oil : the oil itself is processed in such a way that the linoleic glycerides present are transformed into forms which are not so susceptible to atmospheric oxidation or, alternatively, the acids of ground-nut (or similar) oils are submitted to the same treatment and then converted into esters of a suitable alcohol (usually cyclohexanol). Modern substitutes for natural olive oil of the types indicated above are designed to have the necessary resistance to atmospheric oxidation and consequent development of heat, and should replace efficiently the more costly high-grade olive oils for oiling the scoured wool fibres.

Rosin oils and mineral oils are not infrequently blended with oleines or other non-drying oils to produce a cloth oil, but the use of blended oils of this kind is not viewed with approval, because all the lubricant employed must be subsequently removed by scouring with soap solution, and the constituents referred to are removed only with difficulty and are liable to leave oil-stains on the finished cloth, and also to give trouble in subsequent processes of bleaching and dyeing.

An alternative to the use of simple fatty oils or fatty acids as cloth oils, which is, however, more widely applied abroad than in this country, is that of "emulsion wool oils." These consist of partially saponified fats or partly neutralized oleines, and are thus essentially emulsions of fatty oil in soap solution, stabilized frequently by an emulsifying agent such as gum, alginic acid, etc. The sulphated oil soap-emulsions produced on neutralization of the products dealt with in Section V., Chapter VII. (p. 398), are also sometimes used as wool lubricants.

CHAPTER III.—THE USES OF FATTY OILS IN THE LEATHER INDUSTRIES

ANIMAL skins which are to be converted into leather by tanning contain in their fresh state a certain amount of fat in the cells of the skin, most of which has to be removed prior to the actual processing. On the other hand, in order to render the finished leather pliable, and in place of ordinary tanning in special cases, fats are subsequently incorporated with the hides. The chief uses of fatty oils during the fabrication of finished leather goods may be classified under three headings :

(a) "Fulling" of the prepared skins as distinct from tanning ; this procedure is followed when very soft, pliable leather of the "chamois" or wash-leather kind is to be produced.

(b) "Stuffing" of tanned hides to render them flexible, and, to some extent, to aid in their waterproof qualities.

(c) Application of surface-dressings of drying oils in the production of "patent" leather.

The general nature of the application of fats in the leather trades can best be understood by a brief description of the general treatment of hides so far as fats enter into the processes concerned.

The raw hides or skins are first of all scraped mechanically, when hair and adherent matter is removed ; in the latter is included skin grease, which is recovered from the scrapings by rendering them with hot water. The recovered fat, when settled and filtered, is of a cream to pale brown colour and is known as pale skin grease ; it is used as a component of some classes of lubricants and also to some extent in soap manufacture.

In the next place, or without preliminary scraping,

the hides are treated with lime in order to swell them and rupture the cell-structures of the original living tissue. After splitting the limed hides and steeping them in a liquor (known as "bate" or "puer") which contains organic acids (usually produced by acid fermentation of chaff, bran or dung) and thereby neutralizes most of the residual lime, they are washed and may then be "filled" with fatty oil. For ordinary grades of leather this is only mildly applied or may be altogether omitted; but for very soft chamois leather or wash-leather the "fulling" process completely replaces the usual tanning, and is carried on by thoroughly impregnating the prepared hides in special machines with drying oils. The oils most frequently used are the cheaper fish oils, such as cod, herring, or menhaden oil, and the lower grades of whale oil.

The fulled hides are heaped loosely together and allowed to develop a moderate heat, oxidation of the unsaturated oils proceeding within the fibres and a certain amount of adsorption of the oxidized products proceeding at the internal surfaces of the fibres. The result is that the skins become very soft and flexible and also acquire a characteristic yellow or light brown tint. The oxidation of the fatty oil is not complete and the whole is not fixed or permanently absorbed by the fibre. When the fulling process has proceeded to the required extent, therefore, the treated skins are either scoured with a weak carbonate solution or, in more modern practice, are soaked in hot water and then submitted to hydraulic pressure. The rinsings from the presses separate into an aqueous phase and a fatty emulsion known as degras, which contains a certain amount of water. The degras is utilized subsequently, with other fats, in stuffing ordinary tanned leather.

The "Stuffing" Process.—Hides tanned in the ordinary way with bark or synthetic tannins are somewhat inflexible and brittle, and this is compensated for by "stuffing" them or thoroughly impregnating them by rubbing with fatty mixtures. Besides increasing the flexibility of the leather by, so to speak, lubricating the internal

surfaces, the filling of the interstices of the fibre with fat lessens its permeability to water considerably.

The materials applied to the tanned leather are known in the trade as stuffing greases. As stated, one of the chief constituents is the degras obtained from the fulling of chamois and wash-leather; this alone, however, is somewhat too soft and is usually compounded with tallow, distilled tallow stearine, distilled fish oil or grease stearines, bone fat, skin grease, or similar fats of suitable consistency, the lower-grade products which are unsuitable for soap or other outlet being frequently quite useful for stuffing greases.

Degras substitutes are also employed to a large extent, the supplies of degras from the goat, pig, and sheepskin soft leathers being insufficient. The substitutes are for the most part "blown" low-grade whale oil or fish oils of the usual kinds, whilst sulphated fish oils and oleines are also utilized. The blown or sulphated oils are mixed with more solid greases of the foregoing types in order to make up the stuffing grease.

Stuffing greases are used for ordinary leather of the coarser varieties, e.g. for use in shoe leather, saddlery, etc. The finer qualities of leather, such as "morocco," "kid," etc., are stuffed with softer oils of a higher grade, and for the best qualities neat's-foot oil is used in large amount.

Patent Leather.—The high gloss of patent leather is due to an external application or enamel of linseed oil "varnish," applied somewhat as follows:

The tanned leather is stuffed with a mixture of degras and fish or linseed oil, dried, stretched, and treated with a little glue solution. Three coats of a special linseed-oil varnish are then applied: the composition of the varnish for each coat is not quite the same, but, substantially, all three consist of good linseed oil which is boiled at 250–280° C. with litharge and manganese borate as driers, together with about 1–5 per cent. of Prussian blue and dark-coloured pigments such as burnt umber or lampblack. According to Morrell and Wood, the object is to produce a polymerized lead drying oil which is hardened by the iron of the Prussian blue.

The first coat of varnish is intended to penetrate the leather slightly so as to cover the surface of the grain with an impermeable film, which receives the subsequent coats. This first coat is known as "daub," and is applied evenly at about 35° C. with a wooden tool, the boiled varnish having been thinned with about 30 per cent. of petroleum spirit; the daubed leather is stoved at 35° C. until dry and then exposed to light and air for a day. The material is then rubbed smooth with pumice and the second coat of varnish brushed on, after which it is stored and aired as before. The final coat is then applied in a thin film to the re-pumiced surface and the finished product exposed to air and light for several days. The action of sunlight is considered to render the film more supple and less liable to crack. At present, as in the case of ordinary varnishes, nitrocellulose compounds in volatile solvents are commencing to compete with linseed oil as enamelling or japanning agents.

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SECTION X.—FATTY LUBRICANTS

Liquid Friction and Solid Contact Friction.—The reduction of frictional resistance in the moving parts of machinery by means of lubricants occurs in two distinct ways. In the case of a cylindrical shaft running in a lubricated metallic bearing at a fair speed, the stationary and moving metal parts are each covered with a stationary film of liquid lubricant and the motion involved is simply that of intermediate planes of liquid shearing over one another ; this type is described as liquid oil-film lubrication. The other form of lubrication is involved when a piece of shafting comes into action from rest, or in the many kinds of gearing such as worm-gear or cogs of various forms in which a complete liquid oil-film which shall entirely separate the metal surfaces cannot be maintained. This is referred to as solid contact friction and is quite different in many respects from simple liquid friction.

Since the resistance to be overcome in liquid oil-film lubrication is that of the shear of layers of the liquid over one another, the friction depends mainly on the *viscosity* of the lubricant under the working conditions of temperature employed ; broadly speaking, therefore, the chemical character of the oil is a subsidiary factor, and high-boiling fractions of mineral oil are most generally used on economic grounds. These oils have few other applications and are accordingly far cheaper than the fatty oils, for most of which abundant other uses exist.

For solid contact friction, however, and probably to a minor extent in viscous lubrication as well, another consideration of quite another kind has to be taken into account namely, the “*oiliness*” of the lubricant. Oiliness is an expressive term which denotes what is meant by the practical

man without defining unduly what he really means ; and indeed it is only in recent years that the academic investigations of the late Sir W. B. Hardy, following the late Lord Rayleigh, and of Langmuir and Harkins in America, have elucidated the essential function of a lubricant oil-film at a solid surface. Completely smooth, absolutely film-free solid surfaces of metal, glass, etc., will grip tightly when pressed together—in other words, the frictional effect is extremely high. Such surfaces cannot be obtained except under very careful conditions, since exposure to the ordinary atmosphere of a room permits them to become covered with a very thin film of oily or greasy material which is sufficient to diminish the friction to a large extent. The function of a lubricant in solid contact friction is, however, connected with its adsorption at the metallic surface in this way, and the work of the investigators mentioned goes to show that the adsorption is due to forces which cannot be distinguished from chemical affinity, that those groups in a liquid lubricant which possess most residual or free chemical affinity are directly adsorbed by and oriented towards the solid surface, and that the adsorbed film produced is only of the order of one molecule in thickness.

The bearing of all this upon the problem of solid contact friction is that it has been found by the experiments of Wells and Southcombe, Lanchester, Archbutt, Deeley, Hyde, and others that the best lubricants for the purpose are those containing oxygenated radicals, and especially the free carboxylic radical. Dunstan and Thole have shown that, amongst mineral oils *per se*, those of the more unsaturated type possess "oiliness" to a greater degree than others, but the other investigations referred to prove clearly that the efficiency of fatty oils in solid contact friction reduction is far greater than that of the mineral oils as a class, whilst efficiencies approaching those of a straight fatty oil can be obtained by blending a mineral oil with up to 25 per cent. of fatty oil, or by substituting for the latter 1 or 2 per cent. of fatty acids of a suitable character. The addition of even 0.1 per cent. of rape oil fatty acids to

a mineral oil vastly improves its efficiency for solid contact work.

The above general remarks are intended to convey some impression of the fundamental properties required in lubrication, and bearing these general problems in mind the present-day application of fatty oils as lubricants may now be considered.

It must be remembered that other practical factors enter into the question, of which the economic values of the various possible lubricants are not the least important. It has already been mentioned that fats are too valuable to be employed as lubricants in place of heavy mineral oils unless there is very good reason for this course. In those cases, again, in which liquid fats are used as oil-film or viscous lubricants, the choice of fat is restricted by several factors. The viscosity of the oil must be suitably high, the oil must remain perfectly clear and have no tendency to deposit solid glycerides under the conditions of use and, above all, it must have no "drying" properties, since the production of gummy or resinous oxidized products during use would render it useless as a lubricant.

General Types of Fatty Lubricants.—The use of fats as lubricants may be divided into the three following main groups :

1. Liquid oil-film lubricants for special or delicate machinery.
2. Solid contact friction lubricants in general use ("blended oils").
3. Semi-liquid oil-film or viscous lubricants for coarse bearings (greases and emulsified fats).

i. Liquid Oil-film Lubricants for Special or Delicate Machinery.—The chief fatty oils used in this way are referred to individually below. In these particular cases mineral oils have failed to replace the fatty oils, which are employed in a highly refined, neutral condition for certain classes of machinery.

Neat's-foot (Trotter) oil, of the best grades, neutral, and clarified by chilling and decanting or filtering in order to

remove any traces of solid glycerides, is largely used for small mechanism such as that of clocks and watches, typewriters, sewing machines, etc.

It is substituted to some extent by chilled lard oil or oleo oil and also by dolphin and porpoise oil.

Sperm oil and arctic sperm oil, after removal of solid spermaceti, are employed on a large scale in the lubrication of light machinery such as textile spindles and looms. Dolphin and porpoise oil, with lard and oleo oils, are also used for this class of machine.

Castor oil has come to the fore of late years as a lubricant for petrol engines, especially those which are liable to be exposed to excessively low temperatures, *i.e.* aeroplane engines. Castor oil has a viscosity comparable with that of a medium heavy mineral oil and in addition has a very low solidifying point, whereas mineral oils tend to congeal at low temperatures. The combination of these two properties has made castor oil an important lubricant of the liquid oil-film type in aircraft, and for this purpose a special quality of the best runnings of the oil, freed as far as possible from both free acidity and traces of solid glycerides, is now produced on a very large scale.

The use of neat's-foot, sperm, and the other fatty oils mentioned above probably persists, contrariwise, mainly because they combine non-volatility, clarity, and oiliness with a lower viscosity than that of most mineral oils: for light or delicate mechanism it is desirable to employ a lubricant which possesses low viscosity and as much "oiliness" as the more viscous kinds of lubricants.

2. Solid Contact Friction Lubricants in General Use—“Blended Oils.”—In contrast to the use of fats as lubricants in the preceding and following classes, fatty materials are now rarely if ever employed *per se* for gearing and similar types of solid contact friction lubrication. The fatty oils are employed in admixture with heavy mineral oils in a wide variety of blended or compounded mixtures, each being manufactured and sold under a trade name. It is impossible to indicate specific examples other than to

state that appropriate and separate blends are produced for use in internal-combustion engines of various types, gas engines, steam turbines, crank cases, steam cylinders, marine engine bearings, etc.

Rape oil is the fatty oil most commonly used in the compounded lubricants, and may form from 5 to 30 per cent. of the mixture, the remainder being made up of mineral oil of suitable properties for the particular lubrication which is to be performed; 10-20 per cent. of fatty oil is probably the average proportion. To a minor extent olive oil, or oleo oil, is sometimes used in place of rape oil, whilst for some purposes, *e.g.* gas-engine oil, a mixture of 5 per cent. rape oil and 5 per cent. coconut oil with 90 per cent. mineral oil has been favoured.

Where the lubricant is to possess very high viscosity, as in marine engine oil, the rape or other fatty oil is frequently thickened by "blowing" with air, as described in Section VIII., Chapter II. (p. 482), before it is incorporated with the correspondingly viscous mineral oil used in such cases.

Wells and Southcombe have patented their observation that the essential factor introduced by the fatty oil is a minute amount of free fatty acid, and have proposed accordingly to replace the 5-30 per cent. of fatty oil by a blend of about 0·5-2·5 per cent. of rape oil or other fatty acids, according to the purpose for which the oil is to be used as lubricant.

3. Semi-Liquid Oil-film or Viscous Lubricants for Coarse Bearings (Axe Grease, etc.).—For the more crude kinds of lubrication such as that of the axles of railway wagons or other vehicles, stuffing boxes at the glands of pistons or rotating shafts in closed vessels, etc., the materials employed usually contain considerable amounts of fatty substances. For these purposes the colour and quality of the fat is not a serious consideration, but it is of course necessary that the grease as finally compounded shall not contain more than a very small amount of free acid.

Greases of this kind are as numerous in the trade as the different brands of compounded lubricating oils of the

previous group, but they consist either of a mixture of fats with or without some mineral oil or, more usually, of an emulsion of fat and soap which, again, may be solely derived from fats (and rosin) or may be also incorporated with mineral oil. For some purposes a solid lubricant, preferably graphite (talc, or mica dust), is also added to the mixture. It is only necessary here to indicate the chief kinds of fatty material which enter into these compositions ; these are somewhat as follows :

Skin greases of different animals are frequently employed ;

Wool grease or wool fat, which contains considerable quantities of cholesterol and is a wax rather than a fat, is also used ;

Bone grease, low-grade tallow, and similar low-grade fats, and

Hydrogenated low-grade fish or whale oils, and a mixture of low-grade tallow and palm oil are also serviceable.

A special class of lubricant, the rosin greases, are derived from rosin by partial saponification of the rosin acids by slaked lime, the whole being emulsified in mineral oil.

The production of lubricant grease from any of these materials is carried out in a simple type of emulsifier or mixer, the fats (invariably containing free fatty acid) being first of all neutralized either with slaked lime or aqueous soda ; the thoroughly emulsified mass is passed through a fine-mesh mechanical screen in order to eliminate any lumps of soap or gritty impurities, and is then well mixed with the appropriate mineral oil in cases when the latter is also used. Most of the greases are stiff and practically solid at the ordinary temperature, and are run into appropriate containers or moulds from the mixer in the warm condition.

Lime soap greases are usually compounded so as to be practically anhydrous, a condition which is specified for many types of coarse lubricant ; in other cases a water-oil emulsion is preferred, and here for the most part the alkali combined in the soap components is soda.

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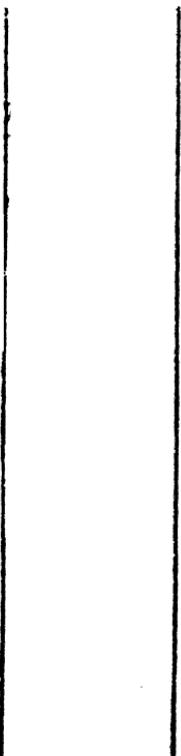
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